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THE

CHEMICAL GAZETTE,

OR,

JOURNAL OF PRACTICAL CHEMISTRY,

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS AND MANUFACTURES.

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TO OUR SUBSCRIBERS.

Our readers have already been informed that with the present Number the Chemical Gazette will cease to have a separate existence. More than seventeen years have passed since this Journal was projected; and during this time we have steadily kept in view the principal object with which it was started, namely, to furnish the English chemist with a *full* and early report of the investigations and discoveries made by those working in the same department of science on the Continent. We were soon convinced that the want we had conceived to exist was not an imaginary one; and the support we have enjoyed for so long a period leads us to believe that we have not altogether failed in meeting it, and that our labours have contributed somewhat to the advancement of chemical science in those countries in which the English language is spoken.

Owing to the increase of other occupations, we have for some time past found it impossible to devote that attention to the work which in justice it required; the appearance of a new *weekly* Journal devoted to the same objects, and which promises to be conducted with considerable ability, seemed therefore to us a favourable opportunity for relieving ourselves of a task we no longer had leisure to perform efficiently, and we assented, though not without some feelings of regret at parting with what

to us had become an old friend, to the incorporation of the "GAZETTE" with the "NEWS." Hoping that our readers will benefit by the change, and that the NEWS and GAZETTE conjoined may meet with the same kind support we have so long experienced, we now take our leave, sincerely thanking those, both in this country and in the United States, who have contributed to our success by their subscriptions and their friendly advice.

December 13th, 1859.

THE

CHEMICAL GAZETTE.

No. CCCLXXXIX.—January 1, 1859.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Picric Acids and some of its Salts, with an Advantageous Modification of one of the Processes for obtaining it. By M. Carey Lea, *of Philadelphia.*

Picric, or properly trinitrophenylic acid may be referred, according to the views of Gerhardt, to the type of water H^2O^2, in which one atom of hydrogen has been replaced by an atom of the hypothetical radical trinitrophenyle, $C^{12}H^2X^3$. Pisani has succeeded in forming the chloride of this radical and its amide, or ammonia in which one atom of hydrogen has been replaced by it*.

Picric acid, whether crystallized in thin laminæ from water, or in long prisms from alcohol, is, when pure, of a very pale yellow. Its alkaline salts, when uncontaminated by foreign matters, are of a perfectly pure yellow.

The colour of these alkaline picrates varies very much with the specimens of acid with which they are made; the potash-salt varies through every shade from yellow to yellowish brown, or to chestnut with a golden glitter, and so with the ammonia-salt. It is a little remarkable that picric acid when first obtained from new sources has been twice described as a new acid, the chrysolepic acid of Schunck and the picranisic of Cahours, in both cases apparently in consequence mainly of the difference in the appearance of the alkaline salts of the new acid from that of those formed with picric acid prepared in the usual way.

The chrysolepic acid of Schunck, or picric acid formed by the very prolonged action of nitric acid on aloes, has a greenish shade, and forms a potash-salt differing very much in appearance from ordinary picrate of potash. In place of being pure yellow, it is chestnut-brown, and the play of colours, which with ordinary picrate of potash is red and green, is with it purple and yellow. It appears to form larger needles than the ordinary salt, and is a very beautiful substance. A modification of picrate of potash much resembling

* Liebig's Annalen, vol. xcii. p. 326.

it may be obtained by crystallizing the ordinary salt with the addition of a very small quantity of picramate of potash, an experiment readily made in the following manner: a small quantity of picric acid is introduced into a test-tube, water added and a single drop of solution of protochloride of tin; the whole is boiled, supersaturated with carbonate of potash, boiled again and filtered hot; picrate of potash will crystallize out, of a shade of red-brown, depending as to its colour upon the amount of picric acid reduced by the protochloride of tin, which latter must be employed in very small proportion. A similar experiment may be made with the ammonia-salt, the pure yellow of which is converted to chestnut-brown by the addition of a very small quantity of picramate, and to green by a larger one. The resemblance of the salts thus artifically coloured to the picrates formed with the acid obtained from aloes is so striking, that I was for a long time disposed to believe that the aloes acid salts derived their colour from the presence of picramic acid in extremely small quantity. But as picramic acid is readily oxidized into picric by the action of fuming nitric acid *, the aloes acid ought, by being boiled with fuming nitric acid, to be converted into ordinary picric acid, if the difference between them consisted only in the presence of picramic acid. But this reaction cannot be obtained, whereas the artificially coloured salt above mentioned, by being boiled with a large excess of nitric acid and then supersaturated with carbonate of potash, crystallizes in its ordinary state without the slightest admixture of picramic acid. I have not found any process by which picrate of potash prepared from aloes can be brought to the colour of the pure salt. By boiling with animal charcoal the red-brown becomes a dirty yellow, which is the nearest approach I have obtained to the normal colour.

The picric acid first obtained by Cahours from trinitranisol †, and by him called picranisic acid, has been generally admitted by chemists (with the exception of Gerhardt) to be identical with picric acid, and not merely isomeric with it. It is only difficult to understand how this could ever have been doubted, whether we look to the source of its formation or to its physical characters. Although the crude acid sometimes gives a dark coloured potash-salt, it more frequently at once yields a bright yellow one with all the marked characteristics of picrate of potash.

The process for obtaining picric acid from commercial creosote is an advantageous one. The acid obtained is readily purified, and gives bright ellow alkaline salts.

A number of experiments were made on the old process of

* Of this fact, though called in question by Gerhardt (Chimique Organique, iii. 47), there can, I think, be no doubt.

† In preparing trinitranisol, if the process ordinarily given for obtaining nitranisic acid be followed, a great portion of the product is lost. After acting upon oil of fennel for a sufficient length of time with nitric acid, we are directed to add water to throw down yellowish flocks which are the impure nitranisic acid. I have found that after the complete deposition of the yellow flocks, the mother-water still contains the greater part of the nitranisic acid, and by standing for twenty-four hours deposits it.

decomposing indigo with nitric acid with very various results, probably depending upon the great difference in the composition of commercial indigo. I have seen the ammonia-salt crystallize out clear yellow, and from the mother-water by spontaneous evaporation, a green picrate of ammonia deposited which exactly resembled that above described as obtained by the addition of minute quantities of picramate of ammonia. The indigo process is one of the least advantageous.

It has been frequently stated that the picric acid obtained from salicine is so pure as not to require purification. Gerhardt, on the contrary, states that oxalic acid is also produced in the reaction, and I have found it so.

Dr. Stenhouse first pointed out that the yellow Australian gum resin obtained from the *Xanthorrhœa hastilis* was the most advantageous substance from which to obtain picric acid. This gum, which has not yet reached our markets, is easily procured in London. It varies very much in appearance, some specimens which I have received being very ligneous, others wholly free from woody fibre.

All the processes prescribed for obtaining picric acid from Australian gum, aloes, indigo, &c. (creosote excepted), are similar; they consist in treating the vegetable substance with six or eight times its weight of strong nitric acid in the cold. After the first strong action has ceased, more acid is added, heat is applied and continued for ten or twelve hours, adding acid to supply the place of that driven off. The process is unpleasant on account of the vast volumes of red nitrous fumes thrown off in the earlier stage, and wasteful, inasmuch as more than half the nitric acid used is driven off unaltered. By the following modification of the process, the amount of nitric acid necessary is reduced one-half, and the disengagement of fumes diminished in a still greater proportion. As all the violence of the action is done away with, the fumes may readily be carried off without inconvenience.

Into a flask capable of containing at least two or three quarts, five ounces of Australian gum is introduced in lumps, twelve ounces measure of nitric acid spec. grav. 1·42 or thereabouts, are poured over it, and as soon as the action commences, twenty-five ounces of water (hot is preferable, but not essential), *which must be at hand ready measured*, as the action is very sudden, is introduced. A gentle heat is then applied; for about two hours the mass puffs up very much; and if there is danger of running over, cold water may be added, but as little as possible, and the necessity for using any should be avoided by a due regulation of the heat. By degrees the mass subsides, when the heat may be increased and continued till the bulk of the mixture is reduced to one-half, or even less. Five more fluid ounces of the same acid are then to be added, and the heat continued till the fluid is reduced to where it was before the last addition, and even carried a little further. From four to seven more fluid ounces of nitric acid will be required to complete the operation. After this last addition, the heat is to be continued until

the mixture is reduced to the bulk of four or five fluid ounces. After cooling, this will be found to have become a cake of picric acid more or less solid in proportion to the point to which the final evaporation has been carried.

The whole of this operation may be carried on in the laboratory without a perceptible escape of acid vapour. A cork in the neck of the wide-mouthed flask with a long-necked funnel, and a bent glass tube sufficiently long to reach within a few inches of the bars of a grate or the air-draft of a stove, will effect this object. By inclining the tube, and placing a vessel under its end, a large quantity of nitric acid may be collected, which may be cohobated, and serve to reduce the quantity of fresh acid employed, remembering, however, that it is very weak, having a specific gravity varying from 1·1 to 1·2.

This process might doubtless be extended to other materials, such as aloes, indigo, the refuse of gum benzoin after sublimation of benzoic acid, &c. It does not require more time than the ordinary process.

The purification of the crude picric acid is best effected as follows:—The crude acid is well stirred up with a small quantity of water, which after rest is decanted, and the operation repeated. The acid thus washed is dissolved in boiling water, sulphuric acid added in the proportion of eight or ten drops to each pint of solution, which is boiled for a few minutes, and rapidly filtered through a heated filter. It is convenient to filter into a porcelain dish over a lamp. The picric acid is then neutralized with carbonate of potash, or preferably with solution of crystallized bicarbonate, as a troublesome second filtration is thus saved. When the potash-salt crystallizes out, it is to be thoroughly freed from the mother-water, and recrystallized. If desired to have a very pure product, it may be boiled with animal charcoal and recrystallized several times. The potash-salt is decomposed in a boiling solution with hydrochloric acid, and the picric acid, when thoroughly freed from adhering chloride of potassium, is pure.

In addition to the reducing agents already known to be capable of converting picric acid into picramic, the same effect may be produced by cyanide of potassium, which in the presence of an alkali instantly decomposes picric acid, producing a solution intensely coloured by picramic acid. Manganid-cyanide of potassium gives the same result with the aid of heat. By boiling the solution with the addition of fuming nitric acid, it is decolorized to pale yellow, the picramic acid having exchanged an atom of NH^2 for one of NO^4. This reaction affords an extremely delicate test for the presence of a cyanide.

Picrate of Baryta.—By slow evaporation yields prismatic crystals, which are dichromatic. In the evaporating basin they present the appearance of yellow prisms with red summits.

Picrate of Glucina.—Carbonate of glucina dissolves readily in a hot aqueous solution of picric acid, and by evaporation yields golden-yellow crystalline crusts. By heating on platinum-foil it becomes

orange-red, boils up, and burns with a feeble deflagration, leaving a sooty mark and a loose white ash.

Picrate of Alumina.—Hot solutions of chloride of aluminium and picrate of ammonia, placed in a beaker-glass and left for several days, give beautiful stellar aggregations of crystals which are permanent in the air, and by heating become slightly brown and then detonate. By recrystallization only crystalline crusts are obtained, which no longer detonate by heating, but only deflagrate with a smoky flame.

Picrate of Protoxide of Manganese.—This beautiful salt, the most interesting of all the picrates, is easily formed by dissolving the protocarbonate of manganese in hot aqueous picric acid. By spontaneous evaporation large prisms belonging to the rhombic system are readily obtained. These prisms exhibit the faces $\infty\breve{P}\infty$, $\infty\bar{P}\infty$ with an intermediate prism face, and the terminal planes 0P. The face $\infty\bar{P}\infty$ is sometimes wanting, and no pyramidal faces were found in any of the very numerous specimens examined.

These crystals are distinctly dichromatic; examined by light transmitted through the prism parallel to its axis, they are of a clear pale yellow colour; in any other position they are of a reddish-salmon, varying with the light. If a crystal be held with its prismatic axis vertical, and be viewed horizontally through a Nicol's prism, so placed that the principal section passing through the obtuse trihedral angles of the prism shall be in the same plane as the axis of the crystal, the image is of a fine salmon-red, varying with different specimens. If the same principal axis of the Nicol's prism be turned till it is at right angles to the axis of the crystal, the image becomes clear light amber-yellow.

The picrate of manganese does not appear to be capable of forming double salts with soda or ammonia. A crystal heated on platinum-foil becomes deep red, and then instantly deflagrates so suddenly as to project portions which do not take fire.

Picrate of Protoxide of Iron.—Isomorphous with the manganous and cadmic salts, crystallizing in large greenish-yellow prisms belonging to the rhombic system, and exhibiting the same faces as the manganous salt, viz. $\infty\bar{P}\infty$, $\infty\breve{P}\infty$ with an intermediate prism face, and the terminal planes 0P. The face $\infty\bar{P}\infty$ is also in this, and the isomorphous cadmium-salt, often wanting. It does not, however, appear to possess the dichromatic properties of the picrates of manganese and cadmium, and unless thoroughly protected from the air, peroxidizes gradually on the surface. Even in solution, however, it is sufficiently permanent to be crystallized by spontaneous evaporation in an open evaporating dish; the surface of the solution becomes indeed covered with a film of decomposed salt, but good crystals may be picked out from underneath.

Picrate of Peroxide of Iron.—Picric acid in solution, boiled with freshly precipitated and still moist peroxide of iron, takes up so little of the metal as to give but slight indications with sulphocyanide of potassium. By accurately precipitating picrate of baryta with persulphate of iron and leaving to crystallize by spontaneous evapora-

tion, the perpicrate of iron is obtained in small yellowish-red prisms and yellow needles, which, particularly when examined with a lens, exhibit a beautiful amethyst reflexion. Heated on platinum-foil, it fuses to a red liquid, which grows deeper and deeper in colour until it takes fire and burns with a hissing noise.

Picrate of Cobalt.—The neutral salt is readily obtained by adding a somewhat concentrated solution of chloride of cobalt to a similar one of picrate of soda. If the solutions be hot, the salt crystallizes out by cooling. In this way beautiful amber-brown crystals may be obtained which often extend entirely across the evaporating dish, and which must be freed from adhering chloride of sodium by recrystallization from a small quantity of hot water. This process is more easy and less wasteful than that recommended in the text-books, of digesting picric acid with carbonate of cobalt and separating the neutral from the basic salt by absolute alcohol. Heated on platinum-foil, the picrate of cobalt melts, becoming reddish black, and deflagrates with a white light.

Picrate of Nickel.—Hydrated oxide of nickel readily dissolves in hot aqueous picric acid, giving a yellow solution which yields green crystals by evaporation. By spontaneous evaporation beautiful prisms are obtained, sometimes an inch and a half or more in length. By heat it becomes first yellow, then brown, and finally deflagrates with a brilliant white light.

Ammonia Picrate of Nickel.—This beautiful but very unstable salt is formed whenever an ammoniacal solution of chloride of nickel is mixed with a soluble picrate. I have generally used picrate of baryta for this purpose. An abundant and highly crystalline bright yellow precipitate takes place, which under the compound microscope is found to consist of bundles of transparent acicular crystals. Even cold water in sufficient quantity decomposes this salt. Placed on a filter and washed, the water runs through bright yellow, and after a sufficient time the filter is found to contain nothing but hydrated oxide of nickel, free from any trace of picric acid, converted partly into basic carbonate by exposure to the atmosphere. The wash-water by evaporation yields, as might be expected, crystals of picrate of ammonia. It is therefore evident that the salt, when precipitated, must be washed with the smallest possible quantity of water. Nearly the whole of the picrate of ammonia may be washed out without changing the colour of the precipitate, which becomes a bright yellow meal of hydrated oxide of nickel coloured by a trace of picrate, having undergone no visible change except the loss of its crystalline structure. Heated on platinum-foil, the ammonia picrate of nickel turns brown and deflagrates with a brilliant white light.

Picrate of Protoxide of Chromium.—Chromous acetate dissolved in aqueous picric acid yields a brown solution which by spontaneous evaporation dries up to a crust which shows no trace of crystallization.

Picrate of Sesquioxide of Chromium.—Basic carbonate of chromic oxide boiled with aqueous picric acid gives a greenish solution, which

by spontaneous evaporation affords greenish crusts with no trace of crystallization. But by accurately precipitating the violet modification of sulphate of sesquioxide of chromium with picrate of baryta, and leaving the filtrate to evaporate spontaneously, minute greenish needles are obtained.

Picrate of Zinc.—Carbonate of zinc readily dissolves in hot aqueous picric acid, and the salt crystallizes out in small prisms which effloresce even in well-closed vessels.

Picrate of Cadmium.—Carbonate of cadmium dissolves readily in hot aqueous picric acid, and gives by spontaneous evaporation very beautiful crystals belonging to the rhombic system, and isomorphous with the manganese and iron salts, which it very closely resembles; it is, however, somewhat lighter in colour than the manganese-salt, and possesses its dichromatic properties in a much inferior degree. It is extremely soluble in water, and the crystals gradually effloresce even in well-closed vessels. By continued boiling its aqueous solution deposits a brown powder, probably a basic salt.

Ammonia Picrate of Copper.—This salt bears great resemblance to the corresponding nickel-salt. It is readily obtained by mixing a solution of sulphate of copper in ammonia with an alkaline picrate; an abundant precipitate falls, so bulky that if the solutions are somewhat concentrated, the mixture becomes pasty. Like the nickel-salt, it scarcely bears washing. Boiled with water, a solution of picrate of ammonia is obtained, and brown flakes of oxide of copper deposited. A portion of the salt covered with a large quantity of water and occasionally stirred for a day or two is entirely decomposed, with deposition of blue flakes of hydrated oxide of copper. The freshly precipitated salt examined under a good microscope appears highly crystalline. Its colour is greenish-yellow with a faint reddish shade, and it has much the lustre and general appearance of the dust upon the wings of butterflies. Heated upon platinum-foil, it deflagrates powerfully with a brilliant white light.

Picrate of Peroxide of Mercury.—Carbonate of peroxide of mercury dissolves by digestion in aqueous picric acid, and gives by evaporation brilliant orange-coloured needles, easily soluble in water, and by exposure to air efflorescing to yellow. Heated, it reddens, melts, takes fire, and burns with vivid combustion. The picrate of protoxide of mercury is a greenish-yellow, very insoluble precipitate.

Picrate of Silver is but slightly soluble. Nitrate of silver poured into a solution of a soluble picrate, as picrate of magnesia, causes at first no precipitate, but after a few minutes beautiful radiating clusters of needles form in all directions through the liquid.

Picrate of Urea.—This very beautiful combination is easily obtained by dissolving urea in solution of picric acid. It crystallizes in large fan-shaped aggregations of bright yellow needles, permanent in the air.

Picrate of Quinine.—Alkaline picrates added to solution of sulphate of quinine throw down a bright yellow powder, insoluble in water, but very soluble in alcohol. By spontaneous evaporation of

the alcoholic solution in a beaker-glass covered with filtering paper, small tufts of yellow needles are obtained. The statement of L. L. Bonaparte, quoted in Gerhardt's 'Chemie Organique,' iv. 123, I have not found confirmed. Heated on platinum-foil, it burns quietly with a yellow flame.—Silliman's *American Journal*, Nov 1858.

On Butylactic Acid. *By* A. Wurtz.

By the action of nitric acid upon amyloglycol, the author has obtained a new acid belonging to the lactic series, which he calls *butylactic acid*. 14 grms. of amyloglycol were gently heated with a mixture of 30 grms. of monohydrated nitric acid and 42 grms. of water. A very lively reaction took place. The liquid was evaporated *in vacuo* over a capsule containing lime, when it left a colourless, acid syrup, which was dissolved in water and neutralized by hydrate of baryta. The solution of the baryta-salt was evaporated.

This salt does not crystallize. It dissolves in water in all proportions, and pretty readily in weak alkohol; absolute alcohol does not dissolve it, and æther precipitates it from its alcoholic solution. When dried at 248° F., it contains 39·9 per cent. of barium. The formula

$$C^8\,H^7\,Ba\,O^6$$

requires 39·9 per cent. of barium.

The lime-salt prepared with the acid separated from the baryta-salt is very soluble in water, soluble in absolute alcohol, and insoluble in æther. The aqueous solution, by spontaneous evaporation, deposits the salt in mamillæ. Butylactate of lime dried at 248° F. contains 16 per cent. of calcium. The formula

$$C^8\,H^7\,Ca\,O^6$$

requires 16·2 per cent.

Butylactate of zinc crystallizes in brilliant spangles, soluble in 160 times their weight of water at 59° F., but nearly insoluble in absolute alcohol. These crystals, which undergo no change in the air, lose 11·9 per cent. of water of crystallization at 212° F.; a loss of 11·7 per cent. would correspond exactly with 2 equivs. The dry salt contains:—

	Found.		Calculated.
Carbon.....	34·7	C^8	35·4
Hydrogen....	5·1	H^7	5·1
Zinc	..	Zn	23·9
Oxygen.....	..	O^6	35·6

These numbers agree with the formula

$$C^8\,H^7\,Zn\,O^6.$$

From the preceding it results that the acid obtained by the oxidation of amyloglycol by means of nitric acid, does not correspond with this glycol, but with butyloglycol, which is placed immediately below in the series. This is easily understood. The oxidation of amyloglycol by nitric acid is so energetic, that 2 molecules of car-

bon are detached to become converted into carbonic acid; the rest of the elements remain combined, undergoing the partial oxidation which produces butylactic acid. The author assumes that this acid contains a radical, $C^8 H^6 O^2$ (butylactyle), derived from butyle, $C^8 H^8$, by oxidation, as acetyle is derived from æthyle. Hence the constitution of butylactic acid is expressed by the formula

$$\left.\begin{matrix} C^8 H^6 O^2 \\ H^2 \end{matrix}\right\} O^4.$$

This is the third member of the lactic acid series:—

$$\left.\begin{matrix} C^4 H^2 O^2 \\ H^2 \end{matrix}\right\} O^4, \text{ glycolic acid.}$$

$$\left.\begin{matrix} C^6 H^4 O^2 \\ H^2 \end{matrix}\right\} O^4, \text{ lactic acid.}$$

$$\left.\begin{matrix} C^8 H^6 O^2 \\ H^2 \end{matrix}\right\} O^4, \text{ butylactic acid*.}$$

The author has obtained glycolic acid by the direct oxidation of glycol;

Lactic acid by the slow oxidation of propyloglycol; and

Butylactic acid by the energetic oxidation of amyloglycol, thus verifying the opinion put forward by him a year ago, that the glycols are the alcohols of the lactic acids.—*Comptes Rendus*, June 21, 1858, p. 1232.

On Crystallized Valerianate of Atropine. *By* H. Callmann.

This salt forms perfectly white and light crusts; the crystals appear to belong to the rhomboidal system, and the faces are very brilliant. At a temperature of 68° F. the crystals soften, and at 89°·6 F. they are liquefied. Under the double influence of air and light, they soon acquire a yellow colour. The carbonic acid of the air displaces a certain quantity of valerianic acid, which is recognizable by its peculiar odour.

The crystallized salt presents the various reactions of the salts of atropine and of the valerianates. It is extremely soluble in water, less so in alcohol, and still less in æther. The analysis of the salt, dried *in vacuo* at the ordinary temperature, gave:—

	I.	II.	Calculated.
C	66·40	66·20	66·00
H	8·90	8·81	8·50
O, N	24·70	24·99	25·50

These numbers lead to the formula

$$C^{10} H^9 O^3, C^{34} H^{23} NO^6 + 2HO.$$

Comptes Rendus, September 6, 1858, p. 417.

* Leucic acid is probably another member of this series.

On several New Alcohols. *By* M. Berthelot.

The synthetic investigations made within the last few years establish general alliances of greater and greater precision between the more simple carbonaceous compounds, which are studied in preference by chemists, and that great multitude of natural proximate principles which have hitherto remained out of the pale of classification. It is thus that the group of the alcohols and their derivatives long isolated and limited in a single series, has received an immense extension in consequence of the discovery of the polyatomic alcohols: the most essential principles of the vegetable kingdom, the sugars, mannite, glycerine, the neutral fatty bodies, and a multitude of other analogous substances, are connected, nowadays, by their chemical functions, with a small number of ideas and laws, analogous to those which prevail in the chemistry of the old alcohols, but more varied and more general. Organic chemistry thus has a tendency to become simplified at the same time that it is constantly enlarging.

In pursuing these experiments, destined to define the function and constitution of the natural proximate principles, and to establish between them new and closer relations, I have succeeded in recognizing the real function of many of the most important of these principles.

My investigations relate to cholesterine, to Bornean camphor, to trehalose, to meconine, to æthal, and to the neutral compounds formed by these various bodies with acids. Æthal has long been regarded as an alcohol, and I extend the same chemical function to the various principles which I have just indicated.

In the course of this memoir, as in those which I have published during the last four years, I designate under the name of alcohol, every neutral principle formed by carbon, hydrogen, and oxygen, capable of combining with any acid, with elimination of water, to form neutral compounds, endowed with the property of reproducing their generators by again fixing the elements of water.

I apply to the nomenclature of these compounds the same rule that I have followed in connexion with mannite and the other saccharine matters; the name of the generative alcohol is accompanied by an adjective, indicating the name of the acid and its equivalent proportion, thus tristearic mannite. This rule prevents the employment of those barbarous and hypothetical names too often made use of in the designation of newly-discovered compounds.

Lastly, the new compounds which I am about to describe are prepared by the same general method as the artificial bodies and the compounds of the various saccharine matters with acids; the acids and the bodies which are to react, are heated to 392° F. in sealed tubes for eight or ten hours. Under these conditions the combination generally takes place with facility, in virtue of simple and direct affinities, and without the assistance of those powerful mineral agents, which are such useful auxiliaries in the presence of stable substances, but are better fitted to effect the destruction or molecular modification of more delicate compounds.

I. Cholesterine, $C^{52}H^{44}O^2$.

The compounds of cholesterine with stearic, benzoic, butyric, and acetic acids are obtained, as above stated, at 392° F. To purify them the excess of uncombined acid is first eliminated, following the same course as with the artificial fatty bodies. In this way the neutral compound is obtained, mixed with the excess of cholesterine which has remained free; the whole is boiled with eight or ten times its weight of ordinary alcohol, which easily dissolves the cholesterine and scarcely acts upon the compound; the boiling alcohol is decanted, and the same treatment is repeated five or six times upon the compound which remains insoluble; the latter is then dissolved in boiling æther, which deposits it, in general, in a crystalline form on cooling. According to analysis, the cholesteric compounds are represented by the union of 1 equiv. of cholesterine and 1 equiv. of acid, with separation of 2 equivs. of water. When treated with alkalies at 212° F., they present a much greater resistance than the neutral fatty bodies; nevertheless, after the action has continued for eight or ten days, they are completely resolved into cholesterine and acid, the latter remaining combined with the alkali. I have prepared—

Stearic Cholesterine, $C^{88}H^{78}O^4 = C^{36}H^{36}O^4 + C^{52}H^{44}O^2 - 2HO$, a neutral, colourless matter, crystallizing in small, brilliant needles, far more voluminous than stearine, sparingly soluble in cold æther, and nearly insoluble in ordinary alcohol, even when boiling;

Butyric Cholesterine, $C^{60}H^{50}O^4 = C^8H^8O^4 + C^{52}H^{44}O^2 - 2HO$, a neutral, solid substance, pretty fusible, and slightly soluble in hot alcohol;

Acetic Cholesterine, and

Benzoic Cholesterine, $C^{66}H^{48}O^4 = C^{14}H^6O^4 + C^{52}H^{44}O^2 - 2HO$, a neutral substance, crystallizing in small, brilliant, and micaceous spangles, fusible between 257° and 266° F., and tolerably soluble in æther, but very sparingly soluble in boiling alcohol.

These facts prove that cholesterine is an alcohol analogous to æthal; various facts, in the investigation of which I am engaged, lead me to think that some of its æthers are to be met with in the normal or pathological products of the human œconomy.

Cholesterine may be regarded as the type of a series of monoatomic alcohols represented by the formula $C^{2n}H^{2n-8}O^2$. To this series also belongs cinnamic alcohol, $C^{18}H^{10}O^2$.

II. Æthal, $C^{32}H^{34}O^2$.

As a new application of my processes—I have obtained the stearic, benzoic, butyric, and acetic æthers of æthal,—I have purified and analysed, following the same course as with the compounds of cholesterine—

Benzoic Æthal, $C^{46}H^{38}O^4 = C^{14}H^6O^4 + C^{32}H^{34}O^2 - 2HO$; and

Stearic Æthal, $C^{68}H^{68}O^4 = C^{36}H^{36}O^4 + C^{32}H^{34}O^2 - 2HO$, a very beautiful substance, fusible between 131° and 140° F., and crystallizing in broad, brilliant laminæ resembling spermaceti.

III. Trehalose.

Its compounds are formed in small quantities by heating trehalose to 356° F. with acids. They are isomeric, or perhaps identical with those of glucose. They reduce potassiotartrate of copper. I have prepared *stearic trehalose*, a neutral substance resembling stearine; *benzoic trehalose*, a neutral liquid; *acetic trehalose*, a neutral liquid which is tolerably soluble in water, and endowed with a bitterness like that of sulphate of quinine; and *butyric trehalose*, $C^{14}H^{11}O^{7}=C^{8}H^{8}O^{4}+C^{6}H^{5}O^{5}-2HO$, a neutral, bitter liquid, soluble in æther and alcohol, but very sparingly soluble in water; when boiled with alcohol and muriatic acid, it forms butyric æther.

IV. Meconine, $C^{20}H^{10}O^{8}$.

Meconine heated to 392° F. for a few hours with stearic acid furnished a neutral compound, but in small quantity. The excess of meconine was separated by boiling water, and the excess of acid by slaked lime. The neutral compound may be represented by the formula

$$C^{92}H^{78}O^{12}=2C^{36}H^{36}O^{4}+C^{20}H^{10}O^{8}-4HO.$$

I was unable, from want of material, to check this formula by saponification.

V. Bornean Camphor or Camphol, $C^{20}H^{18}O^{2}$.

Bornean camphor plays the part of an alcohol; I shall designate it, for the sake of brevity, by the name of *camphoric alcohol* or *camphol*. This substance, when heated to 392° F. for some hours with organic acids, combines with them with facility. The excess of free acid is separated, and then the neutral compound is kept in a stove at 302° F. for half a day, when the camphol that has remained free is volatilized. This process applies especially to the nearly fixed æthers; the volatile æthers might no doubt be purified by distillation. I have prepared *benzoic* and *stearic camphol*; they are both neutral, colourless, inodorous liquids, soluble in æther and alcohol, and decomposable by alkalies, with regeneration of the corresponding acids and of camphol. Stearic camphol agrees with the formula

$$C^{56}H^{52}O^{4}=C^{36}H^{36}O^{4}+C^{20}H^{18}O^{2}-2HO.$$

These æthers present a peculiar interest by their relations to various natural bodies. Thus they may be represented by the union of the hydrated acids with the carburet, $C^{20}H^{16}$, that is to say, with that carburet which is so widely distributed in nature, and the multiple isomeric states of which constitute the greater part of the vegetable essential oils. It is possible that some of these æthers may form a constituent part of natural substances, amber, for example.

Camphol is the first example of a series of monoatomic alcohols characterized by the formula $C^{2n}H^{2n-2}O^{2}$.

The preceding substances are not the only ones which I have investigated; but in the other experiments I have been stopped by a want of material, and by the difficulty of purification. At any rate, these results, coupled with those which I have already obtained upon the saccharine matters, and with those of various other experimenters, tend to arrange the majority of the oxygenated, ternary organic substances in a small number of fundamental groups; acids, alcohols, and conjugate bodies formed by the reciprocal union of these principles, such are the categories to which we must henceforward seek to refer the oxygenated, ternary, organic substances. The methods of analysis and synthesis become every day more extended and more exact; they allow us to give a definite basis to our investigations, and to reduce their results to a small number of very fertile and general points of view.—*Comptes Rendus*, August 9, 1858, p. 262.

On Murexide. *By* F. Beilstein.

The murexide employed for the experiments was prepared by treating 4 parts of uramile with 3 parts of peroxide of mercury, in accordance with the process of Liebig and Wöhler. By this means a somewhat larger amount is obtained than by employing equal parts of the materials, as was done by Liebig and Wöhler. The analysis of this murexide dried at 212° F. gave—

C	34·18	16	33·80
N	30·35	6	29·58
H	3·11	8	2·82
O	32·36	12	33·80

Air-dried murexide contains 2 atoms of water of crystallization, which it loses completely in 14 days in the exsiccator.

The formation of murexide from uramile and peroxide of mercury is easily explained by the equation

$$2C^8N^3H^5O^6+2O=C^{16}N^6H^8O^{12}+2HO.$$

The author's investigation, the object of which was to ascertain the nature of murexide, and especially to determine whether it was an amide, has shown that it is not a neutral body, and by no means a neutral salt, but that it is an acid salt, namely acid purpurate of ammonia. The author assumes in it a bibasic purpuric acid, which does not exist in the free state, but becomes decomposed into alloxan and uramile; in this respect it resembles thionuric acid. The author prepared and investigated the following salts:—

Acid Purpurate of Potash, $C^{16}N^5H^4KO^{12}$ or $C^{16}N^5H^3KO^{11}$, HO, was prepared hy Fritzsche's method, and exhibited properties agreeing exactly with those described by the latter. The analysis of the salt dried at 212° F. gave—

C	31·89	16	=96	31·46
N	23·18	5	70	22·93
H	1·51	4	4	1·31
K	..	1	39·2	12·84
O	..	12	96	31·46

This, however, is an acid salt, and when heated to 572° F. loses 1 atom of basic water, corresponding with 2·95 per cent. Fritzsche found the loss of weight at this temperature to be 3·04 per cent.

Acid Purpurate of Soda, $C^{16}N^5H^4NaO^{12}$, was obtained by boiling solution of murexide with nitrate of soda. It formed a red salt, which was difficult of solution and, when dry, contained 8·29 per cent. of sodium. The formula requires 7·96 per cent. Na.

Acid Purpurate of Baryta, $C^{16}N^5H^4BaO^{12}$, was obtained by precipitating a solution of murexide with chloride of barium; it forms a dark green precipitate. Dried at 212° F. it contained 21·27 per cent. Ba; the above formula requires 20·48 per cent.

Acid Purpurate of Silver, $C^{16}N^5H^4AgO^{12}+3HO$, is the silver-salt prepared by Fritzsche. The author has also prepared

Neutral Purpurate of Silver, $C^{16}N^5H^3Ag^2O^{12}$, which separates in a few minutes after a cold saturated solution of murexide is mixed with neutral nitrate of silver, in the form of a fine brownish-red powder. The salt dried at 268° F. gave on analysis 44·91 per cent. of silver.

When a solution of murexide was mixed with nitrate of silver containing ammonia, it acquired a deep violet colour, but became colourless after some time, whilst a deep violet precipitate was deposited. This, when calcined, left 70·32 per cent. of silver. It is therefore a very basic salt, for neutral purpurate of silver requires only 44·91 per cent. Ag. The formula $C^{16}N^5H^3Ag^2O^{12}+4AgO$ requires 68·55 per cent. The salt also appears to be free from ammonia.

In his attempts to prepare purpurate of lead, the author obtained no homogeneous product. Protonitrate of mercury produces a precipitate which is perfectly insoluble in water, when added to solutions of murexide. The fixation of murexide in cotton-printing appears to depend upon the formation of this precipitate. A solution of bichloride of mercury is employed, with which the stuff dyed with murexide is soaked. But murexide only produces a pale red precipitate in a solution of bichloride of mercury. The stuff, however, is then immersed in a bath of oxalic acid and acetate of soda, by which means it acquires a violet tint. It is evident that in this case protopurpurate of mercury is produced; for when a solution of murexide is mixed with bichloride of mercury, oxalic acid and acetate of soda, the same violet precipitate is produced that is formed directly in a solution of murexide by protonitrate of mercury.

Bichloride of Platinum changes the solution of murexide to yellow, without producing a precipitate in it.

Murexan, according to the author, is identical with uramile. The decomposition of murexide by acids is as follows, according to the author:—

Murexide.		Alloxane.		Uramile, murexan.
$C^{16}H^8N^6O^{12}$	$+2HO=$	$C^8N^2H^2O^8$	$+C^8N^3H^5O^6+$	NH^3.

Gerhardt has already included uramile and murexan under the common name of dialuramide.—Liebig's *Annalen*, cvii. p. 176.

On the Conversion of the Nitrogen of Nitrogenous Matters into Nitrate of Potash. *By* MM. CLOËZ *and* GUIGNET.

This conversion is effected by means of permanganate of potash. The permanganate employed was ascertained to contain no nitrate. Several grammes of crystallized permanganate were converted by sulphurous acid into a mixture of sulphates of manganese and potash, which contained no trace of nitrate.

As has already been stated, ammonia in excess reduces permanganate of potash in the cold, and forms nitrate of potash. But if an excess of permanganate be added and the whole boiled, the nitrate itself is converted into nitrate of potash. In this, as in all the following experiments, the authors have produced at least 1 gramme of crystallized nitre.

Aniline immediately reduces permanganate of potash with a great evolution of heat. Carbonate and oxalate of potash are produced, but only traces of nitrate.

With quinine, the reaction commences in the cold, but is only completed by boiling. It furnishes carbonate and nitrate of potash, and the potash salt of an acid which appears to be new.

Cinchonine is acted upon with more difficulty than quinine.

Cyanogen immediately reduces permanganate of potash in the cold. This is also the case with hydrocyanic acid and cyanide of potassium. In these three cases, nitrate of potash was readily obtained.

The authors think that the action of permanganate of potash upon cyanogen may be employed in the analysis of gaseous mixtures, for example, to separate cyanogen and carbonic acid which has no action on the permanganate, and this is also the case with oxide of carbon, protoxide of nitrogen, &c. Deutoxide of nitrogen, on the contrary, is absorbed in the cold and forms nitrate of potash.

Compounds containing sulphur and cyanogen furnish sulphate and nitrate of potash. This is the case with the body called *sulphocyanogen* by some chemists, which is obtained by the action of chlorine upon sulphocyanide of potassium.

Nitroprussiate of soda is also oxidized very easily, with formation of nitrate of potash. Ferrocyanide of potassium merely passes to the state of ferridcyanide, which resists the action of the permanganate.

Urea is oxidized with great difficulty; after boiling for a whole day, it only furnishes small quantities of nitrate.

Gelatine is readily acted upon in the cold, forming carbonate and nitrate of potash, besides a peculiar salt of potash, which acquires a bright red colour when heated to 392°—572° F.

Pyroxyline is acted upon when boiled, as are also nitronaphthaline and nitrobenzine. In these three cases a considerable quantity of crystallized nitrate of potash was obtained.

Nitronaphthaline also furnished a salt presenting the characters of phthalate of potash, the product which is obtained when naphthaline is oxidized by permanganate of potash.

Nitrobenzine furnished a salt crystallizing in large rhomboidal laminæ, containing an acid which is but sparingly soluble in cold water.

Of course the oxidation of the nitrated derivatives may furnish products different from those obtained by the oxidation of the bodies forming these derivatives. The oxidation of the nitrated derivatives may even be more easy than that of the original substances.

In general it is difficult to foresee whether a given body will reduce permanganate of potash with more or less difficulty. Thus oxide of chrome, precipitated, washed, and dried at the ordinary temperature, reduces the permanganate in the cold, forming chromate of potash and oxide of manganese. By ebullition the reduction is complete in a few minutes, which it would have been impossible to predict from the known properties of hydrated oxide of chrome.—*Comptes Rendus*, November 2, 1858, p. 710.

Note on the Combinations of the Hydrocarbons with Picric Acid. *By* M. Fritzsche.

In studying several products of the distillation of coal, I have found that many hydrocarbons, both solid and liquid, are capable of combining with picric acid. This combination produces well-crystallized bodies, by means of which we may easily deduce the formulæ of these substances, which, owing to their apparent neutrality, could hitherto only be arrived at with difficulty, and sometimes even with but little certainty. I have already described (Bull. de l'Acad. de St. Pétersb.) four such compounds, those of benzine, naphthaline, and two other solid hydrocarbons which are represented by the formulæ

$$C^{28}H^{10} \text{ and } C^{38}H^{18}.$$

The first of the two bodies, of which I have just given the formulæ, is a colourless substance, and forms with picric acid crystals of a deep and intense red colour; it probably represents either anthracene or pyrene, but I have been embarrassed in recognizing it as one or other of these in consequence of the few characteristic differences contained in the descriptions of these bodies inserted in chemical treatises. For a similar reason I have hesitated in giving a name to the hydrocarbon, $C^{38}H^{18}$, which has been recently discovered by M. Knauss at Archangel, in the products of distillation of wood-tar, for it is very probable that this body may be identical with some other hydrocarbon already described. All these circumstances have shown me the necessity of a new comparative examination of all the solid hydrocarbons discovered up to this time; and as this investigation, with which I intend to occupy myself very shortly, would be much facilitated by the study of specimens of these bodies obtained from their actual discoverers, I have to beg those chemists who may have such specimens in their possession, to be kind enough to communicate them to me.

It is not only the hydrocarbons that combine with picric acid, but

also some oxygenated products of the distillation of coal; I shall only cite here phenic acid and a neutral solid body, which I shall study as soon as I return to St. Petersburg. With regard to the products of the distillation of coal in general, this is an inexhaustible source of beautiful products; and I have recently obtained from it a new neutral body, crystallizing in tablets of a fine greenish-yellow colour, like that of the salts of uranium. This body, upon which I cannot yet furnish other details, is probably only a new hydrocarbon.—*Comptes Rendus*, November 8, 1858, p. 723.

On Rumicine. By Karl von Thann.

The object of this investigation was to show the identity of rumicine with the chrysophanic acid discovered by Rochleder and Held in *Parmelia parietina*.

Rumicine was first prepared in 1831 by Buchner and Herberger, in an extremely impure state, and described by them under the name of lapathine; they extracted the roots of *Rumex obtusifolius*, first with æther and afterwards with alcohol, and separated the lapathine from the latter extract; this contains so small a quantity of rumicine that they did not even recognize its extremely sensitive reaction with alkalies.

In the year 1834 Geiger prepared the substance, to which he gave the name of rumicine, in a pure state from the root of *Rumex patientia*. He prepared an alcoholic extract of the root, and this, when diluted with water, threw down an insoluble body. The ætherial extract of this body furnished a brownish-yellow residue when evaporated, and this, by repeated washing with alcohol and finally with æther, was converted into a deep yellow powder with a greenish tinge (resin).

From dry and peeled roots Geiger obtained a far finer rumicine, which, as he remarks, "was undistinguishable by the eye from the rhabarbarine previously obtained without nitric acid, &c. (from the root of rhubarb); it also behaved chemically exactly like that body." Afterwards he purified the rumicine by digestion with nitric acid and hydrated oxide of lead in solution in æther; the rumicine thus obtained was, as Geiger says, of a beautiful bright yellow colour, with many crystalline particles.

Geiger also obtained rumicine from *Rumex obtusifolius*, and remarks that this plant contains very little of it. Geiger is therefore the true discoverer of rumicine, and on first preparing it called attention to its near relation and probable identity with rhabarbarine.

In 1841 Riegel investigated the root of *Rumex obtusifolius*, and obtained rumicine from it in a tolerably pure state, by various methods, including those of Geiger and Vaudin (the latter recommended his method for the preparation of rheïne). At last he prepared rumicine from the ætherial extract of the root, as recommended by Brandes for the preparation of the yellow matter of rhubarb. He distilled off the ætherial extract, filtered the granular

crystalline yellowish-brown mass deposited in the residue, and then recrystallized it several times from alcohol.

The latter method was also followed by the author essentially in the preparation of the rumicine which served for his analyses; but he adopted another mode of purification, because by Riegel's method he only obtained the substance in a very impure state.

The coarsely pounded roots of *Rumex obtusifolius* (*Radix lapathi acuti* of the shops) were extracted by anhydrous æther in a displacement apparatus, and the combined extract distilled on the water-bath, until only a small residue was left. On cooling, a dark brown mass separated from this, which was filtered, washed with a little æther, and then dried between several folds of filtering-paper. When dried, it was boiled with alcohol of spec. grav. 0·833 and filtered; a dark brown body remained on the filter, whilst on the cooling of the hot filtrate, a dingy greenish-yellow mass separated therefrom, which remained greenish even after repeated solution in alcohol and separation, and only exhibited traces of crystallization. As the green resin could not be separated in this way, the alcoholic solution of the substance was precipitated by a large quantity of water; the flocculent, yellow precipitate was separated by filtration, and, after drying, dissolved again in alcohol of spec. grav. 0·833, when a small quantity of a brown body remained undissolved. This operation was twice repeated, but the substance still continued impure.

The final purification was effected by the author in accordance with the process of Rochleder and Held, employed by them in their investigation of the lichens.

For this pupose the substance was treated with a mixture of ammonia and weak alcohol, the filtered solution diluted with water, and neutralized by acetic acid; the yellow precipitate was completely washed with water, and the same operation was repeated; the last precipitate obtained was dried and recrystallized from alcohol; the crystalline mass deposited was again dissolved in æther, and the solution left standing in a loosely covered vessel, in which the rumicine slowly crystallized as the æther evaporated.

The rumicine thus obtained formed a shining crystalline mass of a light golden-brown colour, which was seen under the microscope to consist of distinct, yellow, transparent prisms, apparently belonging to the monoclinohedric system, and exhibit a golden-yellow colour by reflected light. By crystallization from hot alcohol on its cooling, the author obtained rumicine (unfortunately in very small quantity) in the form of a pure yellow, crystalline mass, with a golden lustre. The previously mentioned light golden-brown, crystalline mass was analysed, and gave results agreeing with the formula proposed by Gerhardt for chrysophanic acid, $C^{28}H^{10}O^8$.

C	69·59	69·64	28 = 168		69·42
H	4·36	4·59	10	10	4·13
O	..	..	8	64	26·45

This substance was evidently still contaminated with a small

quantity of a body containing more carbon or less oxygen, which was also indicated by its darker colour.

That rumicine does not merely possess a similar per-centage composition with chrysophanic acid, but that it is also identical therewith, is shown by its behaviour towards reagents.

Rumicine dissolves with extraordinary difficulty in cold water; it dissolves more readily in æther, and still more in strong alcohol. When heated upon platinum-foil, it fuses and emits fumes of an intense yellow colour, whilst a portion remains in the form of a vesicular coal, which, when more strongly heated, burns away without residue; if the same experiment be made in a test-tube, the colder portion of the latter becomes coated with a yellow deposit, which appears crystalline and of a golden lustre under the microscope. In concentrated sulphuric acid, it dissolves with an intense red colour, and, when the solution is diluted, is thrown down again in yellow voluminous flakes. In alkalies, it dissolves very readily, with a splendid dark-red colour (in potash much more easily than in ammonia): it is precipitated without alteration from these solutions by acids. The solution in potash becomes violet-blue, and darker by evaporation. Potash is the best test for rumicine. The ammoniacal solution gives a lilac precipitate with neutral acetate of lead, and a beautiful rose-coloured one with alum.

The alcoholic solution of rumicine gives a reddish-white precipitate with an alcoholic solution of basic acetate of lead (but none at all with the neutral acetate), which is converted into a rose-coloured precipitate by boiling with water. With acetate of copper in alcohol, it gives a blackish-green precipitate, which when diluted and carefully mixed with a few drops of ammonia is converted into a voluminous deep blue precipitate (very different from hydrated oxide of copper), and is soluble with a violet-blue colour in an excess of ammonia.

The reactions of chrysophanic acid agree perfectly with the above.

Besides the method above described, the author also attempted to prepare rumicine by the method recommended some years ago by Rochleder for the preparation of chrysophanic acid; but the solution of potash in aqueous alcohol extracts from the root, together with the very small quantity of rumicine, so many other substances, that the subsequent purification is attended with as much difficulty as in extraction by æther.

There is consequently no doubt that rumicine (also called lapathine) is identical with chrysophanic acid; and the author concludes his memoir with an expression of his conviction that he has wiped away two out of the chaos of names of imperfectly investigated organic compounds.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xxxi. p. 26.

Note on the Decomposition of Cyanide of Mercury by the Iodides of Methyle, Æthyle, and Amyle. *By* M. Schlagdenhauffen.

When alcoholic solutions of cyanide of mercury and iodide of æthyle are left to evaporate slowly, small red crystals are formed.

When the two solutions are boiled together and left to evaporate spontaneously, a slight border of prismatic crystals is also observed at the upper part of the capsule. It seems from this that iodide of æthyle partially decomposes cyanide of mercury, and that iodide of mercury is produced. Under better conditions the author has obtained iodide of mercury and cyanide of æthyle, corresponding with the quantities of cyanide of mercury and iodide of æthyle.

For this purpose he placed in a tube 4·78 grms. of cyanide of mercury, 4·62 grms. of iodide of æthyle, and 30 grms. of alcohol. After the tube had been closed, it was heated in the oil-bath to 248° F. All the cyanide being dissolved, the liquid began to grow yellow, and in half an hour fine yellow crystals were deposited in the interior of the tube, and soon acquired the characteristic red modification of iodide of mercury. The tube was cooled and opened, and the crystals of iodide of mercury separated by filtration. The filtered liquid was distilled, when a small additional quantity of iodide of mercury was deposited, and a product of an alliaceous odour passed into the receiver together with the alcohol. The alcoholic liquid, which is neutral to test-papers, furnished, when treated with potassium, an abundant blue precipitate in presence of a proto-persalt of iron.

Experiment proves therefore that, at a temperature of 248° F. and under suitable pressure, cyanide of mercury is decomposed by iodide of æthyle, and that the double decomposition is effected very exactly.

Two analogous experiments were successfully repeated with the iodides of methyle and amyle. These operations may therefore be summed up in a single general formula,—

$$C^n H^{n+1} I + CyHg = IHg + C^n H^{n-1} Cy.$$

Comptes Rendus, November 8, 1858, p. 740.

On the Separation of Magnesia from Potash and Soda.
By G. G. Schaffgotsch.

A solution of sesquicarbonate of ammonia in excess produces a precipitate in concentrated solutions of magnesia-salts; this is at first flocculent, but becomes crystalline; it was first observed by Fourcroy, and has been analysed imperfectly by Guibourt and Buchholz, and completely by Favre. According to the latter its composition is $NH^4O, CO^2 + MgO, CO^2 + 4HO$, and it leaves 15·9 per cent. of residue when calcined. The same precipitate is produced when 1 equiv. or an excess of caustic ammonia is added to sesquicarbonate of ammonia; it is extremely difficult of solution in this fluid. One part of the salt required 60,000 parts of such an ammoniacal fluid, after shaking 6000 times. The author therefore recommends the separation of magnesia from the alkalies in this way. He communicates a series of experiments, from which it would appear to be completely successful.—Poggendorff's *Annalen*, civ.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Salts of Anisic and Nitroanisic Acids. *By* A. ENGELHARDT.

THE author describes the following anisates:—

Anisate of Potash, $C^{16}H^7KO^6$.—The acid was neutralized with carbonate of potash, the salt obtained was dried, and recrystallized from alcohol of spec. grav. 0·889. It forms fine nacreous laminæ, and contains no water of crystallization. Amount of potassium found 20·63 per cent., calculated 20·60 per cent.

Anisate of Soda.—Pure anisic acid was dissolved in carbonate of soda; the salt obtained was dried, and dissolved in boiling alcohol. The alcoholic solution on cooling furnishes shining laminæ of the salt *a*; but when this solution, together with the laminæ deposited in it, is exposed for some time to the air in a capsule, the laminæ disappear, and in their place splendid and rather large crystals of the salt *b* make their appearance.

a. $C^{16}H^7NaO^6+HO$.—Forms transparent, shining, rhombic laminæ. The salt contains 5·11 per cent. of water (calculated 4·92); dried at 266° F., it contains 13·6 per cent. of sodium (calculated 13·22).

b. $C^{16}H^7NaO^6+10HO$.—Transparent crystals, effloresceng very rapidly in the air, which is an obstacle to the determination of their crystalline form; they, however, appear to belong to the monoclinohedric system. When dried at 248° F., the salt lost 33·61 of water (calculated 34·25), and when dry contained 13·36 of sodium (calculated 13·22 Na).

Anisate of Baryta, $C^{16}H^7BaO^6$, is obtained by the evaporation of the aqueous solution in the form of colourless, shining, rather thick tabular crystals. This salt contains no water of crystallization; it is but sparingly soluble in water, and may consequently be obtained by decomposing anisate of ammonia by chloride of barium. It contains 31·09 per cent. of barium. The above formula requires 31·20 per cent.

Anisate of Strontia, $C^{16}H^7SrO^6+HO$.—It is obtained by the precipitation of a strong and hot solution of anisate of ammonia

with nitrate of strontia. The salt forms brilliant laminæ, which lost 4·38 per cent. of water at 284° F. (calculated 4·41), and contained when dry 22·22 per cent. of strontium (calculated 22·48 Sr).

Anisate of Lime, $C^{16}H^7CaO^6+HO$, was obtained by saturating anisic acid with carbonate of lime. The salt is deposited on the cooling of the boiling solution in the form of transparent, elongated laminæ; but by the slow evaporation of the aqueous solution, small, flat, prismatic, transparent crystals are formed. At 338° F. the salt lost 5·33 per cent. of water (calculated 5·0 per cent.); the dry salt contained 11·53 per cent. Ca (calculated 11·69 per cent.).

On treating anisate of baryta and anisate of lime by the method adopted by Piria in the preparation of the basic salicylates, the author obtained no corresponding basic anisates.

Anisate of Magnesia, $C^{16}H^7MgO^6+4HO$, was obtained by saturating anisic acid with carbonate of magnesia. This salt is very soluble in water and alcohol. From the alcoholic solution it crystallizes in flexible needles grouped in a stellate form. When dried at 230° F., it lost 16·93 per cent. of water, and when dry contained 7·32 per cent. of magnesia (calculated 7·36).

Anisate of Lead, $C^{16}H^7PbO^6+HO$, was obtained by the precipitation of anisate of ammonia by acetate of lead. It is a heavy white powder, which dissolves in boiling water, and on the cooling of the solution is deposited in beautiful, thin, nacreous laminæ. When heated to 158° F., it undergoes no change; when more strongly heated to 176°—194° F., it loses its water of crystallization, cakes together, and fuses into a transparent, glassy, yellow mass. The crystallized salt, when heated to 217° F., lost 3·40 per cent. of water; the precipitate obtained by mixing acetate of lead with anisate of ammonia lost 3·5 per cent. of water (calculated 3·41). The crystallized salt contains 39·19 per cent., and the precipitated one 39·91 per cent. of lead (calculated 39·32).

Basic Anisate of Lead, $C^{16}H^6Pb^2O^6+HO$.—A boiling solution of anisate of lead gave a heavy white precipitate with a solution of basic acetate of lead; this was separated from the fluid by decantation, washed with water, and dried under a bell-glass over caustic potash. This precipitate, when examined by the microscope, is found to consist of small tabular crystals. The salt contains 2·48 per cent. of water, and the dry salt 58·16 per cent. of lead (calculated 2·4 of water and 58·03 of lead).

Anisate of Copper.—A solution of anisate of ammonia or soda produces a greenish-blue precipitate with a solution of acetate or sulphate of copper. This precipitate is not homogeneous; it consists of a mixture of anisic acid with a basic salt, so that under the microscope the needles of anisic acid may easily be distinguished from the amorphous basic salt. When washed with æther, the anisic acid is dissolved, and the basic salt remains. In determining the copper in this basic salt washed with æther, the author obtained no concordant results (23·41 and 26·82 per cent. of copper in the salt dried at 248° F.).

The precipitate which is produced by mixing anisate of soda and acetate of copper, dissolves in boiling acetic acid; but after the

cooling of the solution, the anisic acid is deposited in the form of needles, whilst the copper remains in solution.

Nitroanisates.

Nitroanisate of Potash, $C^{16}H^{5}(NO^{4})KO^{6}+2HO$.—This is obtained by saturating nitroanisic acid with carbonate of potash. The solution formed is evaporated to dryness, and the residue recrystallized from alcohol, when the salt is deposited in the form of brilliant, elongated tables. It contains 6·63 and 6·77 per cent. of water, and the dry salt contains 16·62 of potassium (calculated, water 7·1, and potassium 16·62 per cent.).

Nitroanisate of Soda, $C^{16}H^{5}(NO^{4})NaO^{6}+2HO$.—This salt was obtained by saturating nitroanisic acid with carbonate of soda. It crystallizes on the cooling of the hot aqueous solution in the form of yellow, flat needles; from the hot alcoholic solution it crystallizes in fine, yellow needles. The salt contains 7·27 and 7·42 per cent. of water, and after drying at 266°—320° F., 10·04 and 10·42 per cent. of sodium (calculated, water 7·59, and sodium 10·5 per cent.).

Nitroanisate of Baryta, $C^{16}H^{5}(NO^{4})BaO^{6}+4HO$, is procured by mixing anisate of baryta with nitrate of baryta; it forms a white flocculent precipitate. It is nearly insoluble in cold water, but far more soluble in that fluid when boiling. Flakes, consisting of microscopic needles, are deposited from the boiling solution. The salt, when heated to 302° F., lost 11·77 per cent. of water, and the dry salt contained 25·74 per cent. of barium (calculated, water 11·9, and Ba 25·89 per cent.).

Nitroanisate of Strontia, $C^{16}H^{5}(NO^{4})SrO^{6}+4HO$, is a similar salt to the preceding. The air-dried salt, when heated to 287°·6 F., lost 12·5 per cent. of water, and the dried salt contained 17·89 per cent. of strontium. The formula requires water 13·05, and strontium 18·22 per cent.

Nitroanisate of Lime, $C^{16}H^{5}(NO^{4})CaO^{6}+4HO$.—By mixing nitroanisate of soda with chloride of calcium, this salt is obtained in the form of a crystalline precipitate; when recrystallized from water, it consists of flexible, microscopic needles. 0·3063 grm. of the salt, dried in the air, lost 9·4 per cent. of water when heated to 302° F. The dried salt contained 9·19 per cent. of calcium (calculated 9·25 Ca).

Nitroanisate of Lead, crystallizes from water in needles, which contain no water of crystallization, and explode violently when heated to redness.

Action of Anhydrous Sulphuric Acid upon Anisic and Nitroanisic Acids.—Anisic acid was poured into a flask, and this connected with a retort containing Nordhausen sulphuric acid, from which anhydrous sulphuric acid was then distilled. The product formed in the flask was gently heated for some time to render the action of the anhydrous sulphuric acid more complete; the tenacious brown mass obtained was then dissolved in water, and filtered, to separate the undecomposed anisic acid; the solution was saturated with carbonate of baryta and evaporated. By this means it acquired an

acid reaction and deposited a small quantity of an insoluble brown matter, which was separated by filtration, and the solution then left to evaporate spontaneously in the air. In course of time a gelatinous mass, insoluble in water, was deposited from the solution; this was separated, and the solution was boiled with carbonate of baryta, and filtered. A portion of this solution was mixed with a small quantity of alcohol; the brown, tenacious mass thus separated was removed, and the mother-liquor treated with an excess of alcohol, by which means a flocculent white precipitate was obtained. This was washed with alcohol, pressed between bibulous paper, and then immediately placed under the bell of the air-pump over sulphuric acid, because, when exposed to the air, it greedily attracts moisture and deliquesces to a brown fluid, which, when dried over sulphuric acid, gives a transparent, brown, amorphous mass. The salt thrown down by alcohol contains 37·08 per cent. of barium. The formula $C^{16}H^6Ba^2O^6, S^2O^6$ requires 37·32 per cent.

As the properties of this salt render it unfit for investigation, the author endeavoured to prepare neutral soda and lead-salts with the other portion of the solution of the baryta-salt, but could not obtain any crystallizable salt of definite composition. For the preparation of the acid baryta-salt, a portion of the neutral baryta-salt was completely precipitated with sulphuric acid, then mixed with the other portion of the neutral salt, and evaporated, when the baryta-salt was deposited in the form of a white, granular mass. In determining the baryta in this salt prepared at various times (one salt being obtained from a solution which contained a great excess of acid), the salt dried at 338° F. was found to contain 30·34, 30·72, 30·07 per cent. of barium. The formula $C^{16}H^7BaO^6, S^2O^6$, requires 22·87 per cent. Ba.

To judge from the quantity of barium, the formula of the salt analysed might rather be regarded as $(C^{16}H^6Ba^2O^6, S^2O^6 + C^{16}H^7BaO^6, S^2O^6)$; this formula requires 30·8 per cent. of barium.

Mendius not long since obtained an analogous potash-salt of sulphosalicylic acid,—

$$(C^{14}H^4K^2O^6, S^2O^6 + C^{14}H^5KO^6, S^2O^6 + 2HO).$$

Nitroanisic acid is completely decomposed when treated with anhydrous sulphuric acid.—*Bull. de St. Pétersb.*, xvi. p. 289.

On the Composition of the Native Minerals containing Tantalic Acid. *By* H. Rose.

Tantalic acid has hitherto only been found in the tantalites of Finland and France, and in the yttrotantalite of Ytterby in Sweden. In Finland tantalites occur at several places, but especially at Skogböle in the diocese of Kimito and Härkäsaari in that of Tammela.

The tantalites of Kimito were first discovered, and it was in them that Ekeberg found the metal tantalum. They were afterwards more carefully examined, especially by Berzelius. In general they have a less specific gravity than other tantalites, varying only between 7·006 and 7·119, but they contain a very considerable amount of oxide of tin, which was found in two analyses to be 9·67

and 9·14 per cent. It is only by fusing the tantalic acid obtained with a mixture of carbonate of soda and sulphur that the oxide of tin can be separated from the acid; mere digestion with sulphuret of ammonium is not sufficient. These tantalites consist of prototantalates and protostannates of iron and manganese.

The tantalites of Tammela only contain inconsiderable quantities of oxide of tin. In different analyses they exhibited a very similar composition, but may be of very various density, which, however, is generally greater than that of the tantalites of Kimito, varying between 7·311 and 7·943. They consist almost entirely of prototantalate of iron, with insignificant traces of oxide of tin and protoxide of manganese.

Nordenskjöld the younger separates these two kinds of tantalites, and calls that which contains so much oxide of tin ixiolite, retaining the name of tantalite for the mineral from Tammela, which exhibits a simpler composition. According to Nordenskjöld, however, pure tantalite of high specific gravity (7·85), and exactly similar in composition to that of Tammela, also occurs at Kimito.

In France tantalite occurs at Chanteloube, near Limoges; it was discovered and investigated by Damour. It has a high specific gravity (7·64—7·651), and its composition is similar to that of the tantalite of Tammela. In some tantalites of this district, and especially in such as appear to be more decomposed, zirconia also occurs according to Jenzsch and Chandler, and appears partially to replace the tantalic acid.

From the results of the analyses it is difficult to develope a rational formula for the composition of tantalite. In the first place, there is the question whether the whole amount of iron in tantalite is to be regarded as protoxide. It appeared from experiments that only a very small quantity is contained in the mineral as peroxide. But if we assume even in the tantalites of Kimito that stannic acid may replace tantalic acid, with which it possesses the same atomic composition, the amount of oxygen in the two acids stands in an unusual relation to that of the bases. In the tantalites of Kimito this is as 5·2—5·14 : 1; and in the tantalite of Tammela as 4·7 : 1. In the investigated tantalites of France, if we consider the zirconia in them as replacing tantalic acid and oxide of tin (which indeed is rendered probable by recent investigations, from which we may assume that zirconia contains 2 atoms of oxygen to 1 atom of zirconium), the oxygen of the acids is 4·9; 5·07; 5·6 and 4·44 times as great as that of the protoxides of iron and manganese.

In the investigation of the tantalates, the author obtained in the combinations of tantalic acid with potash and soda, compounds of similar constitution to those with protoxide of iron which occur in the tantalites, but at the same time he called attention to the fact that they were not definite compounds. He obtained them from the neutral salts by decomposing these with water, with carbonate of ammonia, and other agencies.

But in the same way protoxide of iron may be washed out of the pure prototantalate of iron from Tammela, by the long-continued influence of water containing carbonic acid, whilst this agent exerts

no solvent power upon tantalic acid. By this means a compound with a greater or less excess of tantalic acid must be formed.

This view will perhaps be regarded as too arbitrary, but the author believes he can substantiate it by the multifarious investigations of the columbites, to which he will hereafter refer. By the analysis of a great many columbites from Bodenmais and from North America, he did not succeed in establishing a probable formula for their composition, for, like the tantalites of Finland, they also contain an excess of acid. But at last the author obtained through Forchhammer of Copenhagen, and Krantz of Bonn, some columbites from Greenland, the external appearance of which showed them to be of great purity and still unaltered by external influences. They also exhibited a different composition; the metallic acid was combined with an amount of bases, the same as that found by the author in other neutral salts of this acid.

The tantalites of Finland have exactly the appearance of the common columbites from Bodenmais and North America. The same thing that applies to the latter, which have evidently not retained their original nature, must also be assumed to apply to the former.

It may therefore be assumed with tolerable certainty that the original composition of the tantalites, especially those of Tammela, is similar to that found by the author in the artificially prepared neutral salts of tantalic acid; the oxygen of the acid is four times that of the bases. The composition may therefore be expressed by $FeO+2TaO^2$. The tantalites of Tammela, and many of those from France, approach this composition more closely than those of Kimito, in which the intermixture of considerable quantities of stannates has probably caused the more advanced decomposition.

The composition of yttrotantalite will be treated of in a subsequent memoir.—*Bericht der Akad. der Wiss. zu Berlin*, 1858, p. 257.

Contributions to the History of Inosite. *By* Dr. Hermann Vohl.

The author has lately proved that unripe beans contain inosite. As this body amounts to $\frac{3}{4}$ per cent. of the weight of the beans, he was able to prepare large quantities of inosite, in order to investigate the properties of this sugar more accurately.

At 41° F. inosite has a spec. grav. of 1·1154. The aqueous solution, saturated at 66°·2 F., has a spec. grav. of 1·0548. 100 parts of such a solution contain—

14·294 inosite.
85·706 water.

Hence 6 parts by weight of water dissolve about 1 part of crystallized inosite. The crystals of inosite contain 16—17 per cent. of water of crystallization. If the solution, saturated at 212° F., be evaporated at that temperature, the substance obtained is free from water. If a solution of inosite be allowed to freeze, the substance separates in white opake crystals, which dissolve but sparingly in the fluid as it thaws; these crystals are anhydrous. From experi-

ments made by Dr. Eichhorn, of Poppelsdorf, inosite possesses no rotatory power.

The concentrated solution of inosite is not syrupous, and undergoes no change if the inosite were pure. Putrefying membranes cause the formation of butyric and lactic acids, as was already observed by Scherer.

Chlorides of sodium and potassium are readily dissolved by solution of inosite. A crystallized compound, such as is formed by grape-sugar under these circumstances, could not be obtained.

Cloetta has stated that inosite furnishes a green precipitate with an alkaline solution of oxide of copper. Pure inosite, according to the author, does not do this; but, on the other hand, he confirms what Cloetta has stated with regard to the behaviour of inosite to a solution of basic acetate of lead.

Thus, if a very dilute solution of pure inosite be mixed with a concentrated solution of the lead-salt, a limpid, transparent jelly is produced, after some time in the cold, but immediately on the application of heat; this, when protected from the air, undergoes no alteration, and does not, as stated by Cloetta, form a crystalline precipitate. No body of constant composition could be separated from this jelly.

When inosite is dissolved in dilute nitric acid and the solution is evaporated to dryness in the water-bath, decomposition only takes place when the fluid is moderately concentrated. Large quantities of nitrous acid are evolved, and on dissolving the residue oxalic acid is obtained by evaporation.

The fluid separated from the oxalic acid was neutralized with carbonate of lime, and the oxalate of lime separated by filtration. The fluid could not be brought to crystallize, and deposited a splendid, purple-red flocculent mass after some time; this was soluble in dilute acids (muriatic, nitric, and acetic), and was precipitated again unaltered from these solutions by ammonia.

Concentrated nitric acid converts inosite into nitroinosite.

Nitroinosite, $C^{12}H^{6}(NO^{4})^{6}O^{12}$, or simplified $C^{2}H(NO^{4})O^{2}$, forms anhydrous crystals; from the alcoholic solution it is obtained in beautifully developed rhombohedra. It is insoluble in water, and when chemically pure, is unaltered by keeping either in moist or dry air.

The author has continued his experiments on the employment of nitroinosite as the explosive ingredient in percussion-caps, and finds that if it can be prepared in sufficient quantities, there is no obstacle to this application of it.—Liebig's *Annalen*, cv. p. 370.

On the Camphenic Series. *By* M. Berthelot.

The relations which exist between the formulæ of Bornean camphor or camphol, $C^{20}H^{18}O^{2}$, of ordinary camphor, $C^{20}H^{16}O^{2}$, and of the isomeric hydrocarbons, $C^{20}H^{16}$, and the artificial formation of ordinary camphor by means of the Bornean camphor, effected by M. Pelouze, have led me to try the inverse experiments, and to form these substances from one another. I have pursued this

endeavour, not taking my stand upon the approximation of the formulæ, which is too often barren of results, but upon considerations relating to the similitude of the molecular states.

In fact, if camphol and ordinary camphor are comparable as regards their physical properties, this is not the case with the hydrocarbons, $C^{20}H^{16}$. Not one of these bodies at present known, affects either the solid state, or the characteristic physical properties of the camphors. But many, if not all, of these hydrocarbons, and especially oil of turpentine, are capable of forming a crystallized hydrochlorate, $C^{20}H^{16}.HCl$, endowed with the general properties of the camphorated substances, and often designated, on account of this circumstance, by the improper name of artificial camphor. It is this hydrochlorate that I have taken as my starting-point. Although my investigations are not yet terminated, I have already obtained certain results, which I think it may be useful to indicate briefly.

I have decomposed the solid hydrochlorate, $C^{20}H^{16}.HCl$, in special conditions adapted to prevent any molecular modification, which had not hitherto been done, and I have obtained a hydrocarbon of the formula $C^{20}H^{16}$, endowed with a rotatory power, volatile at about 320° F., crystallized and fusible at 115° F., exactly resembling the true camphors; this is true *camphene*. Muriatic acid converts it entirely into solid hydrochlorate.

This camphene, oxidized under the influence of platinum-black, becomes converted into a volatile and crystalline substance, possessing the odour and aspect of ordinary camphor, and probably identical therewith; I have not yet completed its investigation.

Lastly, ordinary camphor, $C^{20}H^{16}O^2$, was heated between 356° and 392° F. with an alcoholic solution of soda, in conformity with the method of M. Cannizzaro for converting the aldehydes into alcohols. It furnished camphol, $C^{20}H^{18}O^2$.

I isolated this latter substance in the following manner:—After opening the tubes in which the reaction had taken place, I precipitated the camphorated matter by water*; I pressed it, purified it by sublimation, and then heated it to 392° F. with stearic acid. Under these conditions ordinary camphor does not form any sensible proportion of a neutral compound, whilst camphol forms a large quantity of stearic camphol, which is easily isolated and purified. The body thus prepared possesses the normal composition, $C^{56}H^{52}O^4$. When decomposed by soda-lime at 248° F., it readily regenerates camphol, $C^{20}H^{18}O^2$, with its composition and most essential physical properties. The camphol thus regenerated contains—

C = 77·6.
H = 11·8.

The formula $C^{20}H^{18}O^2$ requires

C = 77·9.
H = 11·7.

These results, which require to be completed by the study of the

* The water retains in solution the soda-salt of a peculiar resinous acid, *camphic acid*, $C^{20}H^{16}O^4$?

rotatory powers, and of the product of oxidation of camphene, will establish between the various camphors and the natural hydrocarbons a totality of experimental relations, founded essentially on the comparative study of the corresponding molecular conditions.—*Comptes Rendus*, August 9, 1858, p. 266.

On Andirine and the Resin of Andira anthelminthica. *By* Theodor Peckolt.

The author has extracted the medicinal resin from the wood of *Andira anthelminthica*, and made some experiments upon its properties.

The wood of this tree is much used in carpentry. In cutting boards from the trunk the workmen are always exposed to very unpleasant attacks, when this hard wood has to be sawn. The sawdust acts upon the body in the same way as tanner's liquor; the workmen are attacked by inflammation of the eyes, the œsophagus contracts, they suffer from unquenchable thirst and a bitter, burning taste; troublesome itching is felt all over the body, and an itch-like exudation is produced. To discover the active principle of this wood, the author examined a portion of sawdust, and attained his object as follows after trying many other more tedious ways.

a. The decoction of the wood, which was of a dingy yellow colour, was evaporated to $\frac{3}{4}$ths of its weight, mixed with hydrate of lime, by which a fine dark brown colour was produced, filtered after standing for 48 hours, evaporated to syrup, and then extracted with alcohol. The residue is a beautiful yellowish-brown colouring matter, to which the author gives the name of *andirine*; according to the experiments of a portrait painter, it is far more beautiful than the so-called nankin, and much finer than the earthy colours, and is applicable both to oil- and water-colour painting, but especially to "glacé." It possesses a strong bitter taste, and has definite medicinal properties. It dissolves readily in alkaline fluids, with a dark reddish-brown colour. The solution gives a blackish-brown precipitate with perchloride of iron. In sulphuric acid it dissolves instantaneously with a dark brownish-red colour, and is not rendered turbid or precipitated by water. In dilute sulphuric acid it becomes reddish yellow, without being immediately dissolved; it is only soluble by long trituration with much dilute sulphuric acid. In nitric acid it becomes yellowish red and dissolves; no change is produced in this solution by water.

In muriatic acid it dissolves with difficulty with a dingy brownish-yellow colour, and is not immediately separated by water, although it becomes turbid, and in course of time a very slight brown precipitate is formed, but the fluid always continues turbid. On the contrary, the solutions in sulphuric and nitric acids, when left standing long with water, constantly become more limpid and beautiful. It dissolves in acetic acid with a fine yellowish-red colour, appearing still redder when mixed with water, when the solution remains clear and limpid.

It is soluble in essential and fatty oils, and mixes readily with

varnish without separating therefrom afterwards. In water it dissolves with a brown colour, but is insoluble in æther and alcohol, whether cold or boiling.

1 pound of sawdust yields about 3 drachms. of andirine.

b. The alcoholic fluid filtered from the andirine, was evaporated, dissolved in æther, and evaporated again; it leaves the acrid bitter resin which will be described below.

c. The wood is digested with alcohol, and pressed, the extract filtered, the alcohol distilled off, and the residue evaporated to the consistence of a thin extract; from this the resin is separated by water. It is dark brown, with a shining fracture when dried, fusible at a gentle heat, becoming soft, tenacious and impressible, but not very viscid in hot water; it dissolves instantly in alcohol with a dark brown colour, tending to reddish; it has a very bitter acrid taste, is inodorous, but evolves a peculiar sweetish odour when heated; it sinks in water, and its alcoholic solution reddens litmus-paper. About a third of it is soluble in æther; the solution colours the skin like tincture of iodine; when evaporated it becomes slimy, and produces a penetrating, burning sensation upon the tongue, which lasts nearly all day. The resin is not dissolved by nitric acid, but becomes converted into a porous mass, without increasing perceptibly in volume; when afterwards triturated, it is soluble in a large quantity of water, and furnished a substance like andirine, but of a darker colour. In sulphuric acid, the resin readily dissolves with a dark brownish-red colour. Chloroform has no action upon it, except that the resin becomes harder. The alcoholic solution of the resin is not precipitated by ammonia, but is rendered more intensely brownish red; when mixed with water, it gives the latter a fine brownish-red colour, and remains beautifully clear and transparent, without the least trace of a precipitate even after a considerable time.

No precipitate is produced by silver-salts.

Acetate of lead produced a slight precipitate resembling andirine. The resin dissolves in alkalies at a boiling temperature.

d. The aqueous fluid separated from the resin in its preparation was evaporated to dryness, the residue treated with alcohol; the fluid separated from the andirine produced, evaporated, triturated with water, and decomposed by sulphuric acid, evolved an extremely agreeable odour, resembling that of œnanthic æther, and after long standing deposited a dark brown powder, which exhibited a resemblance to andirine in its behaviour.

1 pound of sawdust yielded 245 grains of resin, of which about 90 grains were soluble in æther. When dried and powdered, it produces similar symptoms to those caused by the sawing of the wood as above described. The portion of the resin which is soluble in æther appears to be the substance especially injurious to the sawyers, for several experiments made with it gave rise to precisely similar actions; on the other hand, the portion insoluble in æther and soluble in alcohol only produced slight effects.

It cannot perhaps be expected that the body will be much employed as a colour, the quantity of it being too small; but the wood

might probably be advantageously employed in dyeing, as there is no other umber-like vegetable colour that can be obtained so cheaply.—*Archiv der Pharm.* xcvi. p. 37.

ANALYTICAL CHEMISTRY.

On the Detection of Nitric Acid in Solution, with Observations on the Action of Sesquisalts of Iron upon Indigo and Metallic Gold, and on the Neutralization of the Colours of Metallic Solutions. By Henry Wurtz, *of New York City.*

In the course of an investigation now in progress, I have had constant occasion for a good practical method of determining with certainty the presence or absence of nitric acid in small quantities under all possible conditions. The different methods that have been devised for the accomplishment of this important qualitative operation were therefore submitted to examination, and the results obtained seem worthy of being presented in a collected form. The following are the most important of these methods.

1. The *Protosulphate of Iron Test*, or method of Richemont.—This depends upon the well-known reddish or purplish-brown colour produced by the combination of the nitric oxide formed by the deoxidation of free nitric acid by proto-compounds of iron, with the excess of the iron compound. H. Rose, in the last edition of his 'Handbuch*,' ranks this test above all the others, and certainly, when manipulated as there directed by Rose, Richemont's test is scarcely surpassed in delicacy by any other; and when the liquid to be tested is colourless, it is extremely convenient; but unfortunately the colour produced has too little about it that is *characteristic*, and is therefore not certainly recognizable in the presence of many other colours that are of very frequent occurrence. When the quantity of nitric acid is minute, this test requires also a very considerable *length of time*, an important objection.

2. The *Iodine Test*, or method of Higgin†, dependent upon the setting free of the iodine of iodide of potassium by free nitric acid, and formation of the blue starch compound.—When no other free acid than the nitric is present, this mode may be made very delicate and reliable, but when in combination, the nitric must be set free by the addition of sulphuric acid, and as Gay-Lussac long ago observed, sulphuric acid alone gives with a solution of hydriodic acid, or, which is the same thing, with iodide of potassium, free iodine, by the following reaction, $SO^3+HI=SO^2+HO+I$‡. Even in dilute solutions this appears to take place after a time, and when but traces are to be tested for, it is difficult to be certain whether the free iodine indicated is due to nitric acid or to this reaction. With great care, however, I believe that this method may in some cases be made useful, particularly when *free* nitric acid is to be tested for.

In the presence of the least trace of a *sesquisalt of iron*, this

* Vol. i. p. 659. † Chemical Gazette for 1850, p. 249.
‡ Gmelin's Handbuch, i. p. 689.

method is especially fallacious, a fact which has I believe heretofore escaped attention. I find that a deep blue colour is immediately produced when but a minute trace of any such compound is present. In fact, the conclusion that I have drawn from experiment is that a mixture of iodide of potassium and starch solutions when used as a test for sesquioxide of iron in solution, yields in delicacy and sensitiveness to no other mode now in use, and I wish therefore to propose it as a new method of detecting the presence of small quantities of iron. The reaction takes place both in neutral and acid solutions; with sesquichloride of iron it is of course as follows:—

$$Fe^2Cl^3 + KI = 2FeCl + KCl + I.$$

3. *Schæffer's Test*; presented to this Association by G. C. Schæffer at the New Haven meeting in 1851*.—It depends upon the conversion of the nitric into *nitrous acid* by the action of metallic lead, and then treating with yellow prussiate of potash and acetic acid, when a deep golden-yellow colour is developed. This test is extremely delicate, indicating, according to Schæffer, the presence of saltpetre in 60,000 parts of water. As, however, the nature of the yellow compound formed is not precisely known, much less the character of the reaction that takes place, we have no data from which to infer how the presence of other substances, particularly of metallic salts, would modify the result, and I should accordingly hesitate to rely upon it without much previous investigation.

E. W. Davy has since given a somewhat similar process†, dependent on the formation of a *nitroprusside* by heating with yellow prussiate and hydrochloric acid, adding an alkaline carbonate when cold, and then sulphide of ammonium to the filtrate, to produce the familiar brilliant purple colour, by which he detected the 200th part of a grain of saltpetre. It is desirable that this beautiful method should be fully examined, and the modifying influences of all other substances determined, a work which would require much time and labour.

4. The *Brucine Test.*—This depends on the deep blood-red colour given by brucine in contact with free nitric acid, and is lauded as extremely sensitive by Fresenius in his last edition‡. It is necessary to success, however, that the nitric acid should be in a certain state of concentration.

5. The *Gold Test*; founded upon the power of mixtures of nitrates with hydrochloric acid to dissolve *gold-leaf*, by virtue of the chlorine set free, the gold being afterwards detected in the solution by protochloride of tin.

An observation of a very surprising and unexpected character made in connexion with this mode of testing may be appropriately introduced here. I found that solutions containing sesquioxide of iron (no nitric acid whatever being present) have the power to dissolve gold. A solution of pure sublimed sesquichloride of iron was boiled with a fragment of gold-leaf. The liquid soon became turbid,

* Am. Journ. Sci., [2], xiii. 117; Liebig und Kopp's Jahresb. für 1851, p. 625.

† Liebig und Kopp's Jahresbericht, 1853, p. 654.

‡ "Diese Reaction ist ungemein empfindlich." Fresenius's Anleitung zur qualitativen chemischen Analyse, Braunschweig, 1856, p. 175.

from deposition of a basic chloride, as is always the case with neutral solutions of ferric salts, but on acidulating with hydrochloric acid, it cleared up, and the gold had disappeared. Another fragment also dissolved, and so on. The action is accompanied by the production of protochloride of iron, as is easily shown by a solution of ferridcyanide. On filtration, dilution, and treatment with hydrosulphuric acid, the precipitate obtained in the liquid had quite a dark brown colour, and when washed, dried and burned on platinum foil, left a residue easily proved to be spongy gold by burnishing in an agate mortar.

A solution of pure ferric sulphate was also proved to dissolve a little gold, though less readily than the sesquichloride, and to be reduced to ferrous sulphate. Even at the ordinary temperature a solution of the sesquichloride, standing for several days in contact with gold-leaf, gave a green tinge with the red prussiate, indicating reduction. An acid solution of the sesquichloride is also partially reduced by digestion for a few hours on the sand-bath with clippings of *platinum* foil. The solutions of gold are not affected by refrigeration, concentration, dilution or filtration.

I cannot find that this action of gold and platinum upon ferric solutions has been announced before. If observed, it may have been attributed to traces of nitric acid or chlorine still remaining in the liquid, a cause of fallacy not existing when the sublimed sesquichloride is experimented with. Metallic silver, however, has been observed to reduce ferric salts. Gmelin says, "Metallic silver takes up oxygen from a boiling aqueous solution of the sulphate of sesquioxide of iron, so that sulphate of silver and sulphate of protoxide of iron are formed; in the cold, metallic silver precipitates again, and the solution contains only sulphate of sesquioxide of iron as before" *.

It is evident that this behaviour of gold vitiates entirely the gold test for nitric acid in the presence of iron.

6. The *Indigo Test*.—This familiar method needs no description. When hydrochloric acid (or chloride of sodium, as recommended by Liebig†) is added, the bleaching is undoubtedly due to the production of free chlorine, just as the solution of gold under the same circumstances was proved to be by Gay-Lussac‡.

All the five methods previously mentioned depend evidently upon the *production* of a colour not previously existing in the liquid, and which in many cases may be produced by the presence of other substances besides nitric acid, whilst the indigo test depends upon the *destruction* of a colour previously existing, this colour being at the same time a very characteristic one, seldom found in solutions, and belonging to a very stable compound that is well known to be affected only by the most potent oxidizing agents. It seemed to my mind therefore that, other things being equal, the indigo test possesses elements of greater certainty than the others, and furnishes stronger *positive* evidence of the *presence* of nitric acid, though some others may give stronger proof of its *absence*. I set myself to work

* Gmelin's Handbuch, i. p. 128.

† See H. Rose's Handbuch, last edit., i. p. 664.

‡ Liebig und Kopp's Jahresbericht, 1847–48, p. 389.

therefore to investigate the indigo test, and ascertain the circumstances which can modify its action.

I quickly discovered, as announced in a former paper, with surprise I must admit, that like the gold test, it is wholly fallacious in the presence of compounds of *iron*. A solution of pure neutral sesquichloride of iron was found to bleach indigo powerfully, with formation of protochloride. The iron solution used was freshly prepared from green crystals of the sublimed sesquichloride*. Excess of hydrochloric acid does not affect the result. A solution of pure ferric sulphate made by evaporating the sublimed sesquichloride with excess of pure sulphuric acid until free from chlorine, also bleached indigo powerfully; and when a small excess of indigo was added so that the liquid had a perceptibly bluish tint after long boiling and cooling, crystals of pure chloride of sodium being added produced no further change after renewed ebullition, thus showing that the bleaching power of the sesquisulphate is little, if any, inferior to that of the sesquichloride. Red prussiate indicated also in this case a reduction to ferrous sulphate†.

When iron then is present in a liquid to be tested by indigo, it is necessary to precipitate it first, and test in the filtrate after addition of excess of acid. For this precipitation I have recommended in a previous paper the use of *ammonia*, but since that was written the idea has occurred that the presence of ammoniacal salts may possibly interfere in some way with the reaction, although it may be difficult to understand how. An experiment, however, in which two parallel trials were made, everything else being equal, but in the one case a large quantity of sal-ammoniac (free from iron) added, seemed in its result to justify this apprehension. It is *safer*, therefore, until this point is more distinctly determined, to precipitate the iron in every case with *carbonate of soda*. And when ammoniacal salts are already present, the ammonia may easily be expelled by evaporation with excess of carbonate of soda before testing.

Besides ferric solutions, the following substances were found to have the power of bleaching indigo.

Terchloride of Gold, after evaporation to dryness with a large excess of hydrochloric acid, to remove all possible traces of nitric acid, gave a solution which bleached indigo very largely when boiled with it, gold being reduced and deposited, partly as a metallic mirror upon the sides, and partly as a black powder at the bottom of the test-tube. When boiled with a large excess of indigo so as to remain still blue, then filtered, and the blue colour destroyed by nitric acid, the liquid was not affected by hydrosulphuric acid, and therefore no longer contained any gold.

* It was observed that such a solution, after exposure to the *light* for some weeks, contained traces of protochloride, confirming an observation of Osann to the same effect (Liebig and Kopp's Jahresb., 1855, p. 406). Such a solution must therefore be kept in the dark. I may remark here also that it is advisable not to *filter* such a solution through paper, as it was found, after standing for a short time in contact with purified filter paper, to give a green colour with the red prussiate.

† It may be added here that some other vegetable colours were tried, such as acid solutions of litmus, logwood and cochineal, and found to be likewise readily decolorized by sesquichloride of iron.

Bichloride of Platinum, freed in the same way from all nitric acid, bleached indigo powerfully, with production of a very deep brown colour (protochloride of platinum), no precipitate being formed.

Bichloride of Tin, made by passing chlorine gas through a solution of the protochloride to saturation, adding some hydrochloric acid, evaporating to dryness, and heating the residue until it volatilized strongly in white fumes, to expel all excess of chlorine, gave a solution which bleached indigo readily and copiously even *in the cold*. Acidulation with hydrochloric acid did not affect the action.

Pure *Arsenic Acid*, having been evaporated in solution twice with hydrochloric acid to ensure absence of nitric acid, left a crystalline residue which still contained much arsenic acid, for its solution gave with nitrate of silver the brick-coloured precipitate, but which apparently retained also hydrochloric acid in some form of combination. On boiling the aqueous solution of the residue with indigo solution no bleaching action could at first be obtained, but on addition of a little hydrochloric acid the blue colour, though slowly and with some difficulty, vanished.

It is scarcely necessary to remark that all substances which evolve chlorine, iodine or bromine, with muriatic acid, will also bleach indigo, such as KO^3, BaO^2, Ce^2O^3, the *chromates*, the *deutoxide* and salts of the *sesquioxide of manganese*, *manganates* and *permanganates*, *chlorates*, *perchlorates*, *iodates*, *bromates*, *deutoxide of lead*, and the *sesquioxides of nickel* and *cobalt*.

A mixture of deutoxide of manganese with dilute sulphuric acid bleaches very strongly.

There are a few other substances which interfere, although in another way, with the reaction. These are those bases which give precipitates with the sulphuric acid of the indigo solution, such as *baryta*, *strontia*, *lime*, and *oxide of lead*. Such precipitates, by making the liquid milky, render the change of colour during the bleaching less discernible; and moreover, it was found that the indigo, being insoluble in other acids, all goes down with the insoluble sulphate, so that the filtered liquid is colourless. These bases are readily removed, however, at the same time as the iron, by precipitation with carbonate of soda and filtration, before applying the test.

I now come to a class of difficulties which at first sight seemed less easy to obviate. These are the cases in which the *colour* of the liquid to be tested approaches more or less to that of the indigo solution itself. This occurs with solutions of *cobalt*, *nickel*, *copper*, *chromium*, and *uranium*. The mode devised for overcoming this was perfectly successful in every case. It consists of an expansion of the happy idea of Dr. Gibbs (founded upon an observation of Mauméné*) in applying Crum's test for manganese to cobalt and nickel solutions.

The chlorides of cobalt and nickel are used reciprocally, after the manner of Dr. Gibbs, to neutralize the colours of each other. The colour of the mixture, as I have obtained it, is when concentrated

* Liebig and Kopp's Jahresbericht für 1850, p. 156.

rather *grayish* than *brownish*, as it is designated by Dr. Gibbs*. This slight residual colour is however of no consequence, as all that is necessary is to get rid of all admixture of *blue* tint, before adding the indigo solution. In working with cobalt solutions it must be carefully borne in mind that the ordinary rose-coloured hydrate of chloride of cobalt is converted *in solution* into the blue anhydrous chloride by admixture with strong hydrochloric acid, or even with the dilute acid on heating, so that in the application of the indigo test to a mixture of chlorides of cobalt and nickel, on heating to effect the bleaching, the liquid usually assumes a blue colour deeper than it had before. If nitric acid is present, however, on cooling the hot mixture by addition of a little cold water, or better by a current of cold water on the outside of the test-tube, the blue colour wholly disappears.

The green colours of solutions of copper, chromium, and uranium are neutralized in the same manner as solutions of nickel, with chloride of cobalt. In the case of copper, it must be remembered that, as Gladstone has shown†, chloride of copper, like chloride of cobalt, differs in colour according to the quantity of water it is combined with, being in dilute solutions *blue*, but on admixture with strong muriatic acid or on heating, assuming a peculiar *greenish* tint. Now it is only the *green* chloride which neutralizes the chloride of cobalt, so that it is necessary to have sufficient muriatic acid present to ensure the existence of the copper-salt in the green modification, at least while the liquid is *hot*. The colour produced is then very similar to that obtained with the chlorides of cobalt and nickel. In the green-yellow solution of hydrochlorate of uranic acid, the green tint is perfectly obliterated by chloride of cobalt, a light *salmon* tinge being produced which does not interfere with the indigo test. A solution of chloride of chromium is precisely similar in its action to one of chloride of nickel, the resultant colour with chloride of cobalt being *identical* in appearance. A concentrated green solution of protochloride of iron is also rendered almost completely colourless by a little chloride of cobalt, but this is of course a matter of no importance in connexion with the indigo test‡.

* The chloride of cobalt used was chemically pure, having been prepared by the elegant method recommended by Gibbs and Genth in their late "Researches on Ammonia-cobalt Bases" (Chemical Gaxette, 1857, vol. xv. p. 141, &c.), which consists in igniting the violet crystals of the *hydrochlorate of purpureocobalt*, dissolving the residual mixture of chloride and sesquioxide of cobalt in dilute muriatic acid, and expelling the excess of the latter by evaporation. The solution has an extremely rich rose colour. The chloride of nickel used was also prepared with care, and was of high purity.

† Liebig and Kopp's Jahresbericht, 1855, p. 414.

‡ A few other observations were made upon the effects of mingling coloured solutions. The nitrates of cobalt and nickel when mixed in proper proportions neutralize each other just as the chlorides do. With the chloride of nickel and the nitrate of cobalt the neutralization is probably more perfect than when the two chlorides are used. With chloride of cobalt and nitrate of nickel the resultant colour was rather brownish than grayish. The nitrates of copper and cobalt did not seem to be entirely complementary, for on gradually mixing their solutions, the red colour of the excess of the cobalt compound began to appear before the blue of the copper solution had entirely vanished, giving a violet tinge to the mixture. On adding a little muriatic acid, however, the copper became converted into the green modification of the chloride, and every trace of blue disappeared,

In conclusion, to describe the general *mode of manipulation* which I adopt, having found it to add materially to the delicacy and reliability of the test. The liquid to be examined is treated, when any interfering substance is present, as above recommended. If neutral, chloride of sodium is added, instead of muriatic acid, to avoid dilution. If carbonate of soda has been used to precipitate iron, lead, baryta, &c., it is better to *concentrate* somewhat before acidulating with hydrochloric acid. Indigo solution (which should also be strong) is then added until a feeble blue tint (best perceived by holding the test-tube *inclined from* the operator on a piece of white paper) is communicated. The mixture is then warmed, and concentrated oil of vitriol added *cautiously* (to avoid explosive ebullition) with constant agitation. If but traces of nitric acid be present the bleaching may not take place for some minutes, or until a considerable quantity of oil of vitriol has been added. If the oil of vitriol be free from iron and nitric or nitrous acid (which latter two contaminations may be removed by previous boiling with a little

leaving the liquid with the peculiar gray colour. With nitrate of copper and chloride of cobalt also, no perfect neutralization could be effected, but the same gradual passage of one into the other presented itself. Addition of muriatic acid however produced the same effect as before. These observations, and others that I have made, have an obvious bearing upon the question of the manner of interdistribution of two acids and two bases in a solution together, and promise to furnish us with a new and valuable means of investigating this important problem. The subject will therefore be resumed at a future opportunity.

There does not seem to be much present prospect of devising any substitute for the expensive chloride of cobalt for nullifying blue and green colours, at least in the indigo test. The colour of the *manganese* chloride is too feeble. *Permanganic acid*, which approaches in colour to cobalt solutions, is of course inapplicable. Some experiments with permanganic acid gave, however, interesting results. On throwing a little mineral chameleon into very dilute acetic acid, a rich amethyst-coloured solution is immediately formed, with effervescence from escape of oxygen. This solution destroys the green colour of chloride of nickel as perfectly as chloride of cobalt, the resultant tint moreover being extremely similar; with chloride of chromium in certain proportions an approximate colour was produced, but in whatever proportions the two were mixed, a trace of residual red or blue was always left; with chloride of copper a fine deep violet-blue colour, like that of the ammonia-sulphate, was produced.

I desire here to urge upon the attention of chemists this general subject of the mode of interference of colours with each other when in admixture. It seems to me to present a wide and highly promising field of research, the exploration of which would lead to valuable practical results, and probably furnish us with explanations of many phænomena at present considered obscure. Indeed, results of the latter kind have already been foreshadowed and exemplified by the investigations of Gorgeu upon the colours of manganese compounds (Chemical Gazette, vol. xi. p. 248), which explain perfectly the discrepant observations previously made upon these colours, by the interfering colours of impurities. In connexion with such investigations a *scale of colours*, founded upon fixed natural standards, if such a thing could be devised, would of course be of great importance. The modifying influences exerted upon the colours of *precipitates* by the presence of other substances precipitated with them is another branch of the subject fully worthy of special investigation, and would probably lead us to new modes for the qualitative detection of certain substances.

I have made attempts to obtain crystallized double chlorides corresponding to the neutral tinted mixtures of chloride of cobalt with the green and blue chlorides, but have obtained only negative results. The cobalt chloride crystallizes out separately, or at least only mechanically mixed with a little of the other chloride. It would be very interesting to determine quantitatively the *proportions* of the several other chlorides which produce the neutral tint with that of cobalt.

oxalic acid, after the method of Löwe), it is not necessary that it should be otherwise pure. After the bleaching-point has once been reached, if a fresh portion of indigo solution be added, it will generally be bleached *immediately*. In this way I detect practically and certainly one part of NO^5 (as saltpetre) in 25,000 parts of water. In 50,000 parts the reaction is no longer distinct, and the liquid must be concentrated after addition of excess of carbonate of soda. The function of the sulphuric acid is not merely, as appeared to me at first, to appropriate the water present, and produce a *quasi-concentration*, for chloride of calcium cannot be successfully substituted for it. It seems probable that in the presence of a large excess of sulphuric acid, Gay-Lussac's NO^2Cl and Cl^2 are formed, instead of NO^2Cl^2 and Cl. When this mode of manipulation is used, the presence of ammoniacal salts does not seem to exert any unfavourable influence*.—Silliman's *American Journal for July* 1858.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

A New Mode of making Commercial Caustic Soda. *By* John M. Ordway.

In the manufacture of soda by Le Blanc's process, much trouble is occasioned by the unavoidable presence of unoxidized sulphur compounds in the lixivium of the crude soda or "black ball." In that branch of the business which is most extensively carried on, experience has shown methods by which the difficulty is overcome with tolerable success, and accordingly the manufacturer generally aims to produce a good soda ash as the material from which other desired products are to be made. But many consumers require a caustic alkali, and it is inconvenient and expensive for each one to have special kettles or cisterns to prepare what the soda maker could, with mutual advantage, furnish ready for use. Caustic soda has, therefore, begun to be a regular article of commerce, and the demand would be very great if the price of a good article bore a juster ratio to that of soda ash. To reduce the cost to a minimum, it is evidently necessary that a caustic soda of fair quality should somehow be obtained directly from the crude soda lye, without the preliminary pro-

* Before leaving the subject I must present some further observations on which I cannot but *hope* to found a method of testing for nitric acid in the presence of iron. I find that metallic iron (*pulvis ferri*) reduces ferric to ferrous oxide readily even at the ordinary temperature, whilst nitric acid (free from NO^3), unless very concentrated, does not reoxidize the protosalt. In fact, it is already well known that in dilute acid solutions containing nitric and no nitrous acid, iron decomposes water just as in dilute sulphuric acid, and ferrous nitrate is formed. If then means could be contrived to obviate wholly the interference of atmospheric oxygen during the operation of *filtration*, it would be very easy, by acidulating the liquid to be tested with hydrochloric acid, adding a little protosulphate of iron and *pulvis ferri* in the cold, filtering, boiling the filtrate (during which last operation ferric salt would be formed from the ferrous, at the expense of the oxygen of the nitric acid), and then testing for sesquioxide of iron, to detect nitric acid in the minutest quantities. This would also furnish us with a means of separating qualitatively nitric and nitrous acids.

cess of making a clear desulphurized carbonate. But how this can be done economically, is a problem the answer to which has not yet perhaps been reduced to the fewest possible terms. Yet the following process is but one remove from the greatest conceivable simplicity, while it has been found by actual working on the large scale to be sure and effectual, and so easy of execution that any man of good common sense can, by a few trials, acquire all the necessary experience.

The "black balls" made in the usual manner are broken up and fully exhausted by a serial lixiviation, so as to make a solution standing at 15° Beaumé. A stronger liquor cannot be made fully caustic. The solution is heated to the boiling-point and treated with milk of lime prepared beforehand by slacking lime with about six times its weight of water. Three pounds of lime fully suffice for each cubit foot of the lye.

The resulting carbonate of lime, after thorough draining, may be dried by waste heat, and used in making more "black balls."

The clear caustic solution is to be evaporated till it stands at about 45° B.—any salts that may fall being dipped out from time to time To a quantity of this thick red liquor contained in a cast-iron kettle, so set as to admit of being strongly and uniformly heated, we now add as much fine sesquioxide of iron as shall somewhat exceed in weight the amount of dry hydrate of soda contained in the liquor. By a little practice one can soon learn to guess quite correctly at the quantity of oxide required for any particular kettle. There should be so much that when the mixture is dried down with constant stirring it may become a dry substance, and not fuse at a heat just below dull redness. During this drying operation, ammonia is given off in abundance, resulting perhaps from the breaking up of the cyanides commonly present in crude soda. Peculiar, but slight and not unpleasant odours, also arise from the decomposition of the organic impurities of the water used in lixiviation. At last, when the water is all driven off, the mixture rapidly absorbs oxygen, and from a black or dark brown becomes rust-coloured throughout. The fire is now smothered, and the roasted product, after standing in the kettle an hour or two with an occasional stirring, is thrown out into a clean iron vessel. As soon as the kettle is cold enough to be in no danger of cracking, it is filled again with a fresh charge, and, excepting these intervals of cooling, the work is continued night and day without intermission.

The rust-coloured powder, when a sufficient quantity has accumulated, is treated with hot water so as to get a solution standing at about 30° B. This liquor, after standing till it has become perfectly clear, is drawn off and boiled down, by successive gradations, till all the free water is expelled. Soon after the commencement of the evaporation, saline matter begins to fall, consisting of sulphate, sulphite, and carbonate of soda, and this deposit—which should be dipped out as it accumulates at the bottom—continues to form as long as the solution remains at 32° B. Afterwards some chloride of sodium falls, if there is any present, but when the strength gets beyond 36° B. there is no further deposition. The first kettle of the set, or the melting kettle, which should be of cast iron, is kept full

till the solution indicates 42° B., and is then finished off without more filling, since the liquor froths a great deal towards the last, and must have plenty of room to spread itself. Finally, the fire is urged till the hydrate of soda is fused, and, if the mass shows any redness indicative of imperfect roasting, a few handfuls of nitrate of soda are cautiously thrown in to ensure complete oxidation. It seldom takes more than one per cent. of nitrate to destroy any remaining sulphide. When the melted soda has become quiet and a little of it poured out on a cold iron plate shows by immediate solidification and its white colour that all is right, the whole is ladled out into iron moulds, from which it is transferred as soon as cold to air-tight casks. When the operations have been conducted with ordinary care, the product is white or a little grayish, and is pure enough for all common uses.

The main feature of this process is an oxidizing operation, in principle not very unlike the roasting of pyritous ores. But the sulphurets of the heavy metals can be roasted, *per se*, while sulphuretted hydrate of soda, it being by itself fusible at the requisite heat, has to be mixed with an inert substance to reduce it to the dry and porous state, and so render its particles entirely and speedily accessible to atmospheric oxygen. And this is why the brown mass must not be allowed to melt. Oxide of iron seems to be peculiarly suitable for drying up the caustic alkali and separating its particles; and as the same oxide will serve over and over again indefinitely, we need only enough to last till the first lots used are exhausted of alkali and drained and are ready to be used again. There is no need of drying it. Venetian red is a good form of the oxide, but I have always used a pure earthy hæmatite that had first been calcined and ground. It is quite possible that oxide of manganese, free from silica, would do as well, and probably a mixture of the two oxides would do better than either by itself.

It may not be amiss to mention that hemispherical cast-iron kettles, 4 feet 4 inches in diameter and half an inch thick at the sides and three-quarters at the bottom, have been found by long trial to be very suitable both for roasting and for melting. In such a kettle 500 pounds of caustic soda may be finished off at once. Larger kettles would be hard to manage, and smaller ones would cause a loss of time.

This production of caustic soda may be advantageously carried on in connexion with the manufacture of a better quality of soda-ash by a method sometimes resorted to. A solution of carbonate of soda cannot be made stronger than 32° B. Accordingly the crude soda lye when evaporated retains in solution all the caustic soda and sulphide of sodium and deposits a very good carbonate, which is dipped out, drained, and calcined for soda-ash. When the liquor shows by increasing in density beyond 32° B. that the carbonate has all fallen, it can be transferred to other kettles, evaporated till it gets very dense, and then mixed with oxide of iron and dried down. The roasted product will give a good caustic soda by solution, decantation, evaporation, fusion, and deflagration.—Silliman's *American Journal*, November 1858.

THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Platinocyanide of Æthyle. *By* KARL VON THANN.

THE author first endeavoured to prepare this body by the action of iodide of æthyle upon platinocyanide of silver. Even at the ordinary temperature the yellow colour of iodide of silver made its appearance after the mixture had stood for several days; to complete the process, the tube was heated in the water-bath, when the fluid disappeared almost entirely in a few hours; the substance was treated with strong alcohol; the filtrate, when evaporated *in vacuo*, only left a very small quantity of a yellowish, dichroitic (yellow and violet) residue, so that the æther could not be isolated in this way. Probably the platinocyanide of æthyle formed is contained in the yellow substance which is insoluble in alcohol, combined with the iodide of silver to an insoluble compound.

This yellow residue was suspended in alcohol and decomposed by sulphuretted hydrogen gas. The fluid filtered from the sulphuret of silver thus produced was evaporated in the water-bath, when it left a brick-red amorphous residue, which was very soluble in water and in alcohol, deliquescent in the air, and possessed an extremely unpleasant taste and odour (like mercaptan). With nitrate of silver the aqueous solution gave a reddish-brown precipitate, like hydrated peroxide of iron, and with nitrate of mercury a dark blue, caseous precipitate, which acquired a bright red colour in spots by exposure to the air. This brick-red substance is probably a sulphoplatinocyanide of æthyle. When ignited, it left 26·9 per cent. of platinum.

As the æther could not be obtained in this way, its preparation was attempted by the treatment of the alcoholic solution of platinohydrocyanic acid with muriatic acid. For this purpose perfectly pure platinocyanide of barium was dissolved in water, and precipitated by nitrate of silver; the precipitate was then thoroughly washed by decantation with hot water, suspended in water, and decomposed by sulphuretted hydrogen, the filtered fluid evaporated to dryness in the water-bath, the residue of platinohydrocyanic acid

dissolved in absolute alcohol (1 part in 10 parts), and then perfectly dry muriatic acid gas was passed into it, by which the fluid is strongly heated, and it is therefore necessary to cool it at first; after cooling, so many small red crystals separated, that the whole fluid solidified into a crystalline paste. The crystals must be rapidly drained and washed two or three times with a very small quantity of alcohol, and then dried on several layers of filtering-paper over sulphuric acid and caustic potash. The mother-liquor furnishes a further supply of crystals when the passage of muriatic acid gas is repeated, but these are considerably smaller and of a less brilliant colour.

The crystals gave the following results on analysis:—

	I.	II.	III.	IV.		
Pt	49·45	49·62	50·07	49·68	1=99	50·00
C	22·75	22·72	24·33	..	8 48	24·24
N	..	..	..	14·09	2 28	14·14
H	3·67	3·64	3·79	..	7 7	3·54
O	..	..	..	..	2 16	8·08

The defectiveness of the analyses is accounted for by the instability of the substance, for, when dried over sulphuric acid and potash, it constantly loses in weight; and it would appear that æthyle is given off in some form (probably as alcohol), whence the loss of carbon in the Analyses I. and II., which are those of a substance which was dried over sulphuric acid and potash until it no longer lost considerably in weight immediately after its separation from the mother-liquor. For Analysis III., the substance employed had been again dissolved in alcohol, and evaporated under the exsiccator, where it was deposited in larger, but not very regular crystals.

The crystals, according to Professor Grailich, belong to the rhombic system, and appear to be isomorphous with those of the platinocyanide of potassium. The colour in the mass is aurora-red, but under the microscope body and surface colours are distinctly decomposed. The body-colour is brown. The absorption is very different, according to the directions in which the vibrations take place in the body. For the vibrations parallel to the longitudinal direction of the prism the crystals are dark brown; pale brownish-red for the vibrations perpendicular to the longitudinal direction. Hence the crystals appear of very various shades of brown, when the lower polarizing prism is removed from the microscope and only the ocular prism is retained; according as the longitudinal directions of the needles scattered in the field coincide with the principal section of the Nicol's prism, or are placed at right angles to it, they appear darker and lighter.

The surface-colour is a light azure-blue, which changes from colourless to dark steel-blue, as the incidences become more and more oblique. The rays which show these colours always possess a plane of vibration parallel to the longitudinal direction of the prism, whatever may be the plane of incidence.

Fluorescence cannot be detected by ordinary daylight, either on

the unaltered substance, or on the decomposed yellowish, sulphur-yellow, brown, or blackish substance.

The body dissolves in alcohol with extraordinary ease; the solution when evaporated over sulphuric acid gives larger, but irregular crystals. The alcoholic solution is perfectly neutral towards litmus paper. The substance also dissolves with great facility in water, but is decomposed at the same time, and therefore acquires an acid reaction; it appears to be decomposed by water into alcohol and platinohydrocyanic acid:—

$$\left.\begin{matrix}PtCy^2\\C^4H^5\end{matrix}\right\} + \left.\begin{matrix}H\\H\end{matrix}\right\} O^2 = \left.\begin{matrix}PtCy^2\\H\end{matrix}\right\} + \left.\begin{matrix}C^4H^5\\H\end{matrix}\right\} O^2.$$

If the aqueous solution be allowed to evaporate in the air, some extremely delicate acicular crystals of a metallic lustre remain; these possess the properties of platinohydrocyanic acid, and decompose the carbonates with effervescence. In æther this substance is only partially dissolved, whilst a slimy yellow residue remains, which does not mix with æther, and probably consists of $PtCy^2$ pt, platinic-cyanide of platinum (pt=$\frac{1}{2}$Pt, commonly called protocyanide of platinum). On evaporation also the same amorphous residue is obtained.

The substance is decomposed with peculiar rapidity in the air. When a small quantity of the crystals is exposed to the air in a watch-glass, they acquire a darker colour at the margin within a few seconds, and in a few minutes they are converted into a brownish-green body; in about twenty-four hours this acquires a golden-brown, metallic colour, and then consists of very fine interlaced needles, which have an acid reaction, and are composed principally of platinohydrocyanic acid.

If the substance be heated in the water-bath, it acquires a citron-yellow colour in a few minutes, and becomes opake; in this case it appears to undergo the same alteration as by long standing over sulphuric acid, except that in the water-bath the decomposition takes place more rapidly and completely, being converted by long heating to 212° F. into anhydrous platinohydrocanic acid.

	Found.	Calculated, $PtCy^2H$.
Pt	65·12	65·13
C^2	..	15·79
N^2	..	18·42
H	..	0·66

This platinohydrocyanic acid has a deep citron-yellow colour, is opake, and still possesses the crystalline form of the platinocyanide of æthyle; it is therefore a true pseudomorph.

If the substance be heated in a test-tube over a spirit-lamp, it also becomes yellow at first, but white after the lapse of a few seconds, at the same time that a strong odour of cyanide of æthyle is evolved, and oily drops of the same substance are condensed upon the colder parts of the tube; if these be washed with alcohol into a small beaker, and the solution be mixed with alcoholic solution of potash,

an abundance of ammonia is evolved, especially on the application of a gentle heat; the propionic acid formed can be set free in the residue, and recognized by its pleasant, penetrating, acid odour.

From these observations it appears that at a temperature not exceeding 212° F., platinocyanide of æthyle containing water undergoes a gradual decomposition, in which an exchange of æthyle and hydrogen takes place, without its radical ($PtCy^2$=platinocyanogen) being destroyed;

$$\left.\begin{matrix} PtCy^2 \\ C^4H^5 \end{matrix}\right\}, \left.\begin{matrix} H \\ H \end{matrix}\right\} O^2 = \left.\begin{matrix} PtCy^2 \\ H \end{matrix}\right\}, \left.\begin{matrix} C^4H^5 \\ H \end{matrix}\right\} O^2,$$

whilst at a higher temperature another decomposition occurs, in which the radical also is decomposed, and a portion of the cyanogen enters into an independent combination with æthyle,—

$$PtCy^2\,C^4\,H^5 = PtCy + CyC^4\,H^5.$$

When heated in an open vessel, the same alteration takes place. At about 572° F., the mass ignites at one spot, and then constantly smoulders away, until at last a pseudomorph of the crystals consisting of platinum remains.

The anhydrous compound $PtCy^2\,Ae$ could not be isolated, although its preparation was attempted in various ways. When heated in the water-bath, the compound, as above stated, is converted into platinohydrocyanic acid; and it is decomposed in the same way by long standing *in vacuo* over concentrated sulphuric acid, and also by standing for months in the exsiccator not *in vacuo*.

A substance treated in the latter way, which after standing for about 3 months, scarcely showed an appreciable diminution of weight, gave the following results on analysis:—

	Found.	Calculated, $PtCy^2C^4H^5, H^2O^2 = PtCy^2H$.	
Pt	61·75	50·00	65·13
C	17·13	24·24	15·79
N	..	14·14	18·42
H	1·83	3·54	0·66
O	..	8·08	..

The substance employed in the analysis was citron-yellow, opake, and dull; it formed a pseudomorph of platinocyanide of æthyle.

As the substance apparently undergoes an alteration when dissolved in æther, the preparation of the anhydrous compound was attempted by mixing a concentrated alcoholic solution of the hydrated substance with æther; at first no alteration took place, but by degrees a turbidity was produced, and at last a yellow amorphous precipitate was separated, which even by long standing did not become crystalline; hence the preparation of the anhydrous æther could not be expected to be attained in this way.

Finally, the author poured a concentrated alcoholic solution of the æther carefully upon sulphuric acid, so that the fluids did not mingle; in a short time a stratum of a red salt separated at the surface of contact, but this soon became partially white from below

upwards, and probably underwent the same change, which the substance is liable to at a high temperature, so that this mode of preparing the anhydrous compound was also obliged to be given up.

The reaction of ammonia upon the hydrated compound is remarkable. When a glass rod, moistened with ammonia, is brought near the crystals, they deliquesce, and if the little drop produced be then examined under the microscope, it is found that in a short time a small yellow crystal is suddenly formed in each drop, and gradually increases in size. These crystals exhibit all the magnificent properties of platinocyanide of ammonium.

But if a very concentrated alcoholic solution of the substance be mixed with 4 or 5 volumes of æther, and ammonia be then added until its odour becomes distinctly perceptible, splendid colourless crystals are produced in the lower aqueous stratum after the mixture has stood for several days; these increase constantly but slowly for several weeks; with a certain oblique illumination, they exhibit a beautiful violet-blue superficial lustre as long as they remain in their mother-liquor, but when dry, they are of a pure white colour, and undergo no change in the air.

The crystals were filtered, washed with æther, dried over sulphuric acid, and analysed. They gave—

Pt	68·91	1=99	69·72
C	..	2 12	8·45
N	19·09	2 28	19·71
H	..	3 3	2·12

The numbers obtained are rather too low, because a small quantity of a brown flocculent precipitate (probably the product of decomposition of the cyanide of ammonium produced at the same time in the fluid) was intermixed with the crystals, and could not be got rid of.

The properties and composition of this substance agree perfectly with those of Buckton's platinopercyanide of diplatosammonium, so that the identity of the two bodies cannot be doubted.

The substance forms very beautifully developed limpid prisms (needles) of 1 or 2 millimetres in length, which are usually grouped in such a manner, that every three of them are united together perpendicularly in the middle, by which they acquire the elegant appearance of a regular little star. They are extremely difficult of solution in cold, but dissolve rather more easily in boiling water; on the cooling of the hot solution they again separate, but far less beautifully crystallized; it would appear that by this means they are partially decomposed, for on recrystallizing they acquire a yellowish colour; if they be boiled for a long time with water, they are completely decomposed, with evolution of ammonia, and at last a yellowish-white, amorphous body, insoluble in water, remains. Solution of potash and ammonia also dissolves the substance when heated. When heated in a test-tube, it evolves ammonia in abundance. The hot aqueous solution furnishes a white precipitate, similar to cyanide of silver, with nitrate of silver; this is soluble in

ammonia, and consists of platinocyanide of silver. When heated in the air, the substance ignites and smoulders away like tinder, until a pseudomorph of the crystals, consting of platinum, is left. The presence of cyanogen in the body cannot be detected by potash, protoxide of iron, and muriatic acid, and therefore its rational formula can not be written $\left.\begin{matrix}\mathrm{Pt}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{N, Cy}$, as that of a simple protocyanide; but it must rather, as Buckton has shown, be regarded as a so-called double salt of cyanide of platinum, consisting of protocyanide of platinum and protocyanide of diplatosammonium. If we assume in the platinocyanides the existence of the compound radical platinocyanogen=($\mathrm{PtCy^2}$), the rational formula of the compound becomes

$$\left.\begin{matrix}\mathrm{PtCy^2}\\ (\mathrm{NH^4})\,\mathrm{PtH^2}\end{matrix}\right\}\mathrm{N}=\mathrm{Pt^2\,N^2\,H^6\,Cy^2}=2[\mathrm{PtCy\,NH^3}],$$

that is to say, platinohydrocyanic acid, in which the metallic hydrogen is replaced by diplatosammonium, $=\mathrm{N}\left\{\begin{matrix}[\mathrm{NH^4}]\\ \mathrm{Pt}\\ \mathrm{H^2}\end{matrix}\right.$.

The filtered mother-liquor of the crystals was distilled in the water-bath, the residue dried at 212° F., then treated with absolute alcohol and filtered (when a considerable quantity of insoluble residue was left), and the solution evaporated *in vacuo* over sulphuric acid, when there remained a reddish-brown crystalline mass, exhibiting all the properties of platinocyanide of ammonium. The crystals first formed, especially at the margin of the capsule, proved to be hydrated platinocyanide of ammonium. The crystals last formed at the bottom of the capsule were platinocyanide of æthylammonium.

Platinocyanide of Æthylammonium dissolves very readily in water and alcohol, and the solution by evaporation in the air leaves long yellow needles, which, in reflected light, exhibit a magnificent violet-blue surface-tint, and a very strong lustre. From this the process of production of platinocyanide of diplatosammonium may be expressed by the equation

$$3\,\mathrm{PtCy^2\,C^4\,H^5}+3\,\mathrm{NH^3}=\left.\begin{matrix}\mathrm{NH^4}\\ \mathrm{Pt}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{NPt\,Cy^2}+\mathrm{PtCy^2\,N}\left\{\begin{matrix}\mathrm{C^4\,H^5}\\ \mathrm{H^3}\end{matrix}\right.+2\,\mathrm{CyC^4\,H^5},$$

or in case of no platinocyanide of æthylammonium being formed,

$$3\,\mathrm{PtCy^2\,C^4\,H^5,H^2O^2}+3\mathrm{NH^3}=\left.\begin{matrix}\mathrm{NH^4}\\ \mathrm{Pt}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{NPtCy^2}+\mathrm{PtCy^2\,NH^4}$$

$$+\left.\begin{matrix}\mathrm{C^4\,H^5}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O^2}+2\,\mathrm{CyC^4\,H^5}+2\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O^2}.$$

Probably both processes go on simultaneously. The separated cyanide of æthyle undergoes a further decomposition by the presence of an excess of ammonia, which has not yet been accurately

investigated. It is possible that in this reaction cyanide of ammonium and æthylammine may be produced:—

$$CyC^4H^5 + 2NH^3 = Cy\,NH^4 + NH^2C^4H^5.$$

In this supposition the author supersaturated the ammoniacal distillate of the mother-liquor of the crystals of platinocyanide of diplatosammonium with muriatic acid, evaporated it to dryness on the water-bath, and treated the residue with a mixture of absolute alcohol and æther; only a small portion of the substance was dissolved, as a great excess of chloride of ammonium was contained in the residue. The ætherial-alcoholic solution left a hygroscopic residue, which contained 61·84 per cent. of chlorine, and may consequently be regarded as a mixture of chloride of ammonium with chloride of æthylammonium; it contained—

$ClNH^4$	$ClN(C^4H^5)H^3$
Cl=66·36 per cent.	42·9 per cent.

But the decomposition might also have taken place in a different mode from that above supposed; thus—

$$CyC^4H^5 + NH^3 = CyN(C^4H^5)H^3.$$

This compound would be the hitherto unknown cyanide of æthylammonium, which, like cyanide of ammonium, is probably very unstable, and might furnish æthylammine as a product of decomposition.

When cyanide of æthyle is kept for a long time, it is decomposed, and cyanogen may then be detected in it by means of potash, protoxide of iron, and muriatic acid, cyanide of ammonium being probably formed; ammonia appears to act upon cyanide of æthyle in a similar way, but in a shorter time.

Very different is the action of dry ammoniacal gas upon dry platinocyanide of æthyle. If an excess of perfectly dry ammonia be conducted over platinocyanide of æthyle in a tube, the red colour of the crystals passes through blue to milk-white, whilst at the same time water is separated, which, however, is evaporated with the current of ammonia in consequence of the elevation of temperature; the residuary white mass is anhydrous platinocyanide of ammonium.

As platinocyanide of ammonium forms the residue of the decomposition of the æther by gaseous ammonia, æthylammine must be evolved:—

$$\left.\begin{matrix}PtCy^2\\C^4H^5\end{matrix}\right\} + 2N\left\{\begin{matrix}H\\H=PtCy^2\\H\end{matrix}\right\} + N\left\{\begin{matrix}C^4H^5\\H\\H\end{matrix}\right.$$

To ascertain whether æthylammine is produced in this experiment, the author repeated it and conducted the gases evolved into muriatic acid; this fluid was supersaturated with ammonia, and evaporated to dryness on the water-bath, when the residue was treated as above with a mixture of alcohol and æther, the solution evaporated, and the chlorine determined in the residue.

The substance proved to be a mixture of chlorides of ammonium

and æthylammonium. The separation of the latter from very large quantities of chloride of ammonium by means of a mixture of absolute alcohol and æther, is therefore very imperfectly successful although in these cases the solvents employed were always freshly prepared and perfectly free from water.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xxxi. p. 13.

On Arbutine. *By* A. Strecker.

In the leaves of the arbutus (*Arctostaphylos uva-ursi*) Kawalier has discovered a body to which he gave the name of arbutine; he determined its formula to be $C^{32}H^{22}O^{19}+2HO$. When treated with emulsine, this body was decomposed into sugar and a new body, to which he gave the name of arctuvine. He explained the formation of this by the equation

$$C^{32}H^{22}O^{19}\text{ arbutine}=C^{20}H^{10}O^{7}\text{ arctuvine}+C^{12}H^{12}O^{12}.$$

Strecker has prepared arbutine in large quantity, and examined it carefully; his analyses gave numbers which nearly agreed with those of Kawalier, but Strecker arrives at a very different formula.

Arbutine, according to him, is $C^{24}H^{16}O^{14}+2HO$, and it loses 1 atom of water at 212° F. When boiled with sulphuric acid, arbutine was decomposed, just as described by Kawalier, into sugar and a second body, which is identical with that called arctuvine by Kawalier. But Strecker shows, by further investigation, that arctuvine is nothing but hydrochinone. It has all the properties of that body as prepared by Wöhler from chinic acid or chinone.

The splitting of arbutine into hydrochinone and sugar is explained by the equation

$$\underset{\text{Arbutine.}}{C^{24}H^{16}O^{14}}+2HO=\underset{\text{Hydrochinone.}}{C^{12}H^{6}O^{4}}+\underset{\text{Grape-sugar.}}{C^{12}H^{12}O^{12}}.$$

Arbutine therefore corresponds with salicine, which may be similarly decomposed into saligenine and sugar:—

$$\underset{\text{Salicine.}}{C^{26}H^{18}O^{14}}+2HO=\underset{\text{Saligenine.}}{C^{14}H^{8}O^{4}}+\underset{\text{Grape-sugar.}}{C^{12}H^{12}O^{12}}.$$

As the formulæ of salicine and arbutine only differ by $C^{2}H^{2}$, the question arises whether these bodies and their derivatives are mutually homologous. Starting from hydrochinone and saligenine, the compounds standing over against each other in the following Table appear to correspond:—

Hydrochinone series.		Saligenine series.	
Arbutine	$C^{24}H^{16}O^{14}$	Salicine	$C^{26}H^{18}O^{14}$
Hydrochinone	$C^{12}H^{6}O^{4}$	Saligenine	$C^{14}H^{8}O^{4}$
Chlorohydrochinone	$C^{12}H^{5}ClO^{4}$	Chlorosaligenine	$C^{14}H^{7}ClO^{4}$
Bichlorohydrochinone	$C^{12}H^{4}Cl^{2}O^{4}$	Bichlorosaligenine	$C^{14}H^{6}Cl^{2}O^{4}$
Trichlorohydrochinone	$C^{12}H^{3}Cl^{3}O^{4}$	Trichlorosaligenine	$C^{14}H^{5}Cl^{3}O^{4}$
Chinone	$C^{12}H^{4}O^{4}$	Salicylous acid	$C^{14}H^{6}O^{4}$
Chlorochinone	$C^{12}H^{3}ClO^{4}$	Chlorosalicylous acid	$C^{14}H^{5}ClO^{4}$.

A number of compounds are wanting in the hydrochinone series which are easily prepared in the saligenine series, whilst, on the other

hand, in the latter some bodies corresponding with the derivatives of hydrochinone are unknown; thus,—

Unknown.....	$C^{12}H^4O^6$	Salicylic acid	$C^{14}H^6O^6$
Unknown.....	$C^{12}H^4O^2$	Salicetine.....	$C^{14}H^6O^2$
Green hydrochinone	$C^{24}H^{10}O^8$	Unknown	$C^{28}H^{14}O^8$
Bichlorochinonic acid	$C^{12}H^2Cl^2O^8$	Unknown	$C^{14}H^4Cl^2O^8$.

Now although many agreements occur in the two series, the author nevertheless thinks that a homology does not appear probable in this case. He expresses the constitution of hydrochinone, chinone, and chinonic acid, replacing the 2 equivs. of chlorine in chloranilic acid by hydrogen, by the following formulæ:—

Hydrochinone $C^{12}H^4O^2\left.\begin{matrix}O^2\\H\\H\end{matrix}\right\}$, or $\left\{\begin{matrix}C^{12}H^4O^2\left.\begin{matrix}H\\H\end{matrix}\right\}O^2.\end{matrix}\right.$

Chinone .... $C^{12}H^4O^2\left.\begin{matrix}\\\\\end{matrix}\right\}O^2$.

Chinonic acid $C^{12}H^2O^4\left.\begin{matrix}\\H^2\end{matrix}\right\}O^4$.

The radical $C^{12}H^4O^2$ would therefore be a biatomic alcoholic radical, which might be converted into the biatomic acid radical, $C^{12}H^2O^4$, by loss of hydrogen and reception of water. In styphnic acid, $C^{12}H^3(NO^4)^3O^4$, we might perhaps have the nitro-compound which would stand in the same relation to hydrochinone as picric acid to phenylic alcohol.

The experiments which the author has undertaken with arbutine are not yet completed, but he has already found that arbutine is converted into chinone and formic acid by brown oxide of manganese and sulphuric acid; when chlorine gas is passed into an aqueous solution of arbutine, it immediately acquires a yellow or red colour, and after some time yellow shining crystalline laminæ separate; these are chlorinated chinone. By this means a mixture of $C^{12}H^2Cl^2O^4$ and $C^{12}H^3ClO^4$ is obtained, and perhaps also more highly chlorinated compounds. Solution of arbutine behaves similarly towards bromine. An interesting nitrated body is obtained by treating arbutine with nitric acid; this appears to be a nitrochinone or nitrohydrochinone.—Liebig's *Annalen*, cvii. p. 228.

On Bibenzoate of Cumole. By J. Tüttscheff.

The chloride of cumole used in the following experiments, which were carried on in the public laboratory of Socoloff and Engelhardt, was prepared from cumole and pentachloride of phosphorus, by the process first adopted by Cahours.

During the action of pentachloride of phosphorus upon cuminic aldehyde, the author remarked that a product containing carbon was always separated. The distillation of the chloride of cumole obtained, also was not effected without some decomposition, which was clearly shown by the separation of muriatic acid, and the coaly residue left in the retort.

The chloride of cumole thus prepared boiled at a temperature of 491° F.

7 grms. of it were gradually mixed with 16 grms. of benzoate of silver in a porcelain capsule, when the reaction took place without evolution of heat. The mass formed was treated with æther, by which means the chloride of silver was separated and the new compound dissolved. The ætherial solution was left to evaporate spontaneously in a cold place, when it gradually became converted into an oleaginous product of a brownish-yellow colour, and in a few days into a hard crystalline mass. The crystals, freed from adherent oil by pressure between bibulous paper, were treated with weak ammonia, and then dissolved in a mixture of alcohol and æther. The crystals obtained from this solution were again dissolved in boiling absolute alcohol; and the pure crystals deposited from this solution were analysed by the author. Three analyses gave the following numbers:—

	I.	II.	III.			
C	77·02	76·86	76·95	48	=288	77·01
H	6·02	5·75	6·02	22	22	5·88
O	16·96	17·39	17·03	8	64	17·11

Hence the composition of bibenzoate of cumole may be expressed by the following empirical formula, $C^{48}H^{22}O^8$, which, when referred to the type of water, corresponds with the rational formula

$$\left.\begin{matrix} C^{20}H^{12} \\ 2(C^{14}H^5O^2) \end{matrix}\right\} O^4.$$

The reaction itself may be explained in the following manner:—

$$2\left(C^{14}\begin{matrix}H^5\\Ag\end{matrix}O^4\right)+C^{20}H^{12}Cl^2=\left.\begin{matrix} C^{20}H^{12} \\ 2(C^{14}H^5O^2) \end{matrix}\right\} O^4+2AgCl.$$

Bibenzoate of cumole crystallizes in colourless, shining, acicular crystals, fuses at 190°·4 F., and cannot be volatilized without decomposition. After fusion it solidifies at a low temperature to a crystalline mass. It is soluble in alcohol, and more readily in strong than weak, and also more in hot than in cold. From a concentrated alcoholic solution it is separated on the addition of water. Æther, acetone, and chloroform dissolve it readily. Ordinary nitric acid shows no action upon it, even when boiled with it. Sulphuric acid gives a deep red solution with it at ordinary temperatures, and this becomes black when boiled. Ammonia and concentrated solution of baryta have no action upon it.

By distillation with caustic potash cuminic aldehyde is separated, whilst benzoate of potash is produced. This was proved by combining the aldehyde with bisulphite of soda. The analysis of the baryta-salt prepared from the benzoate of potash gave 40·20 per cent. of baryta.

The action of chloride of cumole upon freshly precipitated oxide of silver is similar to that of chloride of benzole, the corresponding aldehyde being separated.

By the action of chloride of cumole upon alcoholate of sodium and acetate of silver, copulated compounds are produced; these correspond with those of bibenzoate of cumole.—*Bull. de St. Pétersbourg*, xvii. p. 125.

On the Behaviour of Chloride of Acetyle to Tartaric Acid. *By* F. Rochleder.

The author publishes a series of investigations made by Ballik in his laboratory on the hevaviour of the common acids, citric acid, malic acid, and tartaric acid towards chloride of acetyle. With regard to tartaric acid the following observations were made.

If finely powdered tartaric acid, dried at 212° F., be treated with an excess of chloride of acetyle in a retort, and the action be assisted by a gentle heat, a great quantity of muriatic acid gas is evolved. The volatilized chloride of acetyle is allowed to flow back upon the tartaric acid as it condenses. In the course of a few hours the tartaric acid has entirely disappeared, and if the chloride of acetyle be distilled off in the water-bath, there remains a limpid syrupous fluid which, on cooling, crystallizes in a stellate form. By heating in the water-bath (at a temperature of 185° F.), the acid fuses again. While the acid was kept in a fused state, a current of carbonic acid gas was passed through the retort. After the acid is thus purified from chloride of acetyle and the muriatic acid entirely removed, it appears, when fused, far more thickly fluid, and crystallizes instantaneously, on cooling, in crystals laid over each other like scales, and grouped in the form of rosettes, which dissolve with ease in chloride of acetyle, and separate in acicular crystals when this solvent is evaporated. Litmus-paper is strongly reddened by this substance. Its taste is at first acid, but afterwards distinctly bitter. It is more readily soluble in strong alcohol than in water, but æther dissolves it only in small quantity. If the aqueous solution be evaporated in the water-bath, there remains a syrupous residue which crystallizes with much difficulty. The crystals are acicular; they attract moisture greedily from the atmosphere, and deliquesce. When heated above 212° F., the fused substance becomes brown, evolves an odour like that of burnt paper, and leaves much coal, which burns away slowly. Baryta-water is not rendered turbid by the aqueous solution of this acid. A solution of nitrate of silver produces no precipitate in the aqueous solution; when heated, the fluid becomes brown, and deposits metallic silver in the form of a black powder. Concentrated sulphuric acid dissolves this acid without blackening it. Basic acetate of lead precipitates the aqueous solution of the acid in voluminous white flakes. With baryta, the acid may be combined in two different proportions. If baryta-water be added to the aqueous solution of the acid until the fluid no longer has an acid reaction, and the mixture be then carefully evaporated, a baryta-salt crystallizes in the course of a short time in tabular crystals. If an excess of carbonate of baryta be added to the aqueous solution of the acid, and the solution of the salt be

filtered and evaporated, there remains an amorphous, gum-like mass, which attracts moisture from the atmosphere.

A solution of the acid in water, neutralized by a solution of carbonate of soda, furnishes a salt crystallizing in prisms.

An aqueous solution of the acid, precipitated with basic acetate of lead, furnishes, as already stated, a voluminous, white precipitate. This was collected on a filter, washed with water, suspended in water, and decomposed by sulphuretted hydrogen; the sulphuret of lead was separated by filtration, and the filtrate evaporated in the water-bath. The residue was difficult to crystallize, and the crystals which made their appearance after long standing over sulphuric acid, deliquesced rapidly in the air. If the crystals be fused, the mass does not solidify on cooling; even after standing for a fortnight over sulphuric acid *in vacuo*, it still formed a thick, colourless syrup. The fusion was effected in the water-bath. The baryta-salt of the acid, separated from the lead-salt, is amorphous and deliquescent; its soda-salt crystallizes in warts.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xxix. p. 26.

On Cyanuric Æther. *By* H. Limpricht.

Eight years ago the author commenced an investigation upon the cyanuric æther discovered by Wurtz, and in publishing his results mentioned a beautifully crystallized body of the composition $C^{14} H^{11} N^3 O^6$, that is biæthylocyanuric acid, $\left.\begin{matrix}(C^2 N)^3 \\ (C^4 H^5)^2 H\end{matrix}\right\} O^6$. He has caused this investigation to be continued in his laboratory by Habich. The following results were obtained.

Cyanuric Æther, $C^{18} H^{15} N^3 O^6$, was prepared by the distillation of cyanurate of potash with æthylosulphate of potash. This æther, when boiled with alkalies, is not decomposed directly into carbonic acid and æthylamine, but intermediate products make their appearance. If it be boiled with baryta-water, carbonate of baryta is deposited, but neither ammonia nor æthylamine is set free. If the fluid be evaporated after boiling for half an hour and the removal of the carbonate of baryta, there remains a syrup, which is difficult of solution in water, but readily soluble in alcohol, the composition of which is $C^{16} H^{17} N^3 O^4$. Its production is expressed by the equation

$$C^{18} H^{15} N^3 O^6 + 2HO = C^{16} H^{17} N^3 O^4 + C^2 O^4.$$

If this syrup be distilled, it is decomposed into cyanic æther and diæthylurea.

$$C^{16} H^{17} N^3 O^4 = C^6 H^5 NO^2 \text{ cyanic æther} + C^{10} H^{12} N^2 O^2 \text{ diæthylurea.}$$

If the diæthylurea be treated with dry muriatic acid gas, it is decomposed into muriate of æthylamine and muriate of cyanic æther.

$$C^{10} H^{12} N^2 O^2 + 2HCl = C^6 H^5 NO^2, HCl \text{ muriate of cyanic æther} + C^4 H^7 N, HCl.$$

Muriate of cyanic æther is also formed from cyanic æther and

dry muriatic acid. It is a fluid of a penetrating odour, which acts strongly upon the eyes, and boils at 203° F. without decomposition. With water it is immediately decomposed into carbonic acid and æthylamine.

$$C^6 H^5 NO^2, HCl + 2HO = C^2 O^4 + C^4 H^7 N, HCl.$$

Liebig's *Annalen*, cv. p. 395.

On the Constitution of Hydrobenzamide and Amarine. *By* A. Borodine.

1. If 1 equiv. of hydrobenzamide be heated with rather more than 2 equivs. of iodide of æthyle to 176°—212° F., a turpentine-like mass is formed, and this always contains more or less of a crystallized body, which separates in fine needles. This crystalline body appears to be hydriodate of amarine. The excess of iodide of æthyle employed is expelled by a gentle heat, when about twice the weight of the hydrobenzamide employed is obtained in crude product dried at 212° F.

This dissolves readily in alcohol. A little water is added until a turbidity is produced; the fluid is left to become clear and decanted from the deposit, which has carried down some impurities with it. Nearly the whole of the substance contained in the solution is then precipitated with water. The precipitate forms a thick oil; at the same time a crystalline body sometimes separates, but the greater part of it remains in solution. The precipitated oil is strained through linen, in order to separate the crystals from it, the strained oil is again dissolved in alcohol, and filtered through charcoal, and the solution is evaporated in the water-bath. The body obtained dissolves easily in alcohol, but is sparingly soluble in boiling water. In æther it is insoluble. Concentrated sulphuric acid dissolves it, and acquires a brown colour; on the application of a stronger heat the fluid becomes black, and gives off vapours of iodine. This body fuses readily; at 302° F. it does not appear to undergo any change. From the alcoholic solution nitrate of silver throws down iodide of silver. Hydrated oxide of lead, oxide of silver and potash, likewise remove iodine from it.

After treatment with oxide of lead and oxide of silver, the solution has a sharp and bitter taste, and after purification by animal charcoal and evaporation, leaves a soft, viscous resin. This is scarcely soluble in water, but dissolves readily in alcohol. Æther also dissolves it, although in smaller quantity. The solution in alcohol is precipitated by a solution of silver; the flocculent precipitate thus produced becomes brown by exposure to the air. Concentrated sulphuric acid dissolves this body, and when the solution is heated, it becomes brown and evolves sulphurous acid. If it be heated in a tube closed at one end, it begins to boil; at the same time it is decomposed, and a strongly alkaline fluid distils over. This body may also be prepared by treatment with potash, but the product is then obtained with greater difficulty in a pure state. The

iodide of potassium and the excess of potash may be removed by washing with water.

When purified as far as possible, by treating the solution with animal charcoal, this body has the composition $C^{50}\,H^{28}\,N^2\,O^2$. The analysis gave—

C	86·99	87·40
H	7·98	7·49

This body may be regarded as a double atom of oxide of ammonium, of which 6 atoms of hydrogen have been replaced by 3 equivs. of the biatomic group $C^{14}\,H^6$, and the two others by æthyle.

$$\left.\begin{matrix}NH^4\,O\\NH^4\,O\end{matrix}\right\}\quad\begin{matrix}N\,C^4\,H^5\\(C^{14}\,H^6)^3\,O.\\N\,C^4\,H^5\end{matrix}\quad O.$$

Hydrobenzamide therefore may be regarded as a double atom of ammonia in which all the hydrogen is displaced by 3 equivs. of the biatomic group $C^{14}\,H^6$:—

$$\left.\begin{matrix}NH^3\\NH^3\end{matrix}\right\}\quad N\left\{\begin{matrix}C^{14}\,H^6\\C^{14}\,H^6\\N\,C^{14}\,H^6\end{matrix}\right\}$$

According to this view, hydrobenzamide would be a triatomic ammonia, and the preceding body an ammonium-base. Indeed, the latter behaves like an ammonium-base, for when treated with iodide of æthyle, it is no further æthylized. The products obtained by this means certainly vary a little, according to the duration of the action, but among them there is always a body which, when heated, evolves very irritating vapours, producing tears and headache. There are also resinous bodies which almost always contain iodine, although in variable quantities. The product in this case is the hydriodate $\left.\begin{matrix}N\,C^4\,H^5\\(C^{14}\,H^6)^3\\N\,C^4\,H^5\end{matrix}\right\}I^2$, equivalent to $2\,NH^4\,I$. By the double decomposition of this iodide with sulphate, nitrate and acetate of silver, the corresponding salts are obtained. The sulphate $=N^2\left.\begin{matrix}(S^2\,O^4)\\(C^4\,H^5)^2\\(C^{14}\,H^{16})^3\end{matrix}\right\}O^4$ is not crystallizable, but forms a mass fusing at 212° F. The nitrate, $N^2\left.\begin{matrix}(NO^4)^2\\(C^4\,H^5)^2\\(C^{14}\,H^6)^3\end{matrix}\right\}O^4$, is likewise uncrystallizable; it is equivalent to $2\left.\begin{matrix}NH^4\\NO^4\end{matrix}\right\}O^2$. The acetate also is not crystallizable.

2. If amarine be heated with rather more than 1 equiv. of iodide of æthyle to 176°—212° F., a yellow, solid mass is obtained, which dissolves in alcohol of spec. grav. 0·912. By spontaneous evaporation, this solution furnishes crystals of two kinds.

Long silky needles of hydriodate of amarine first appear; these

are followed by oblique rhombic prisms of diæthylamarine. The action of iodide of æthyle upon amarine is therefore—

$$2(C^{42}H^{18}N^2)+2C^4H^5I=C^{42}H^{18}N^2,IH+C^{42}H^{16}(C^4H^5)^2N^2+HI.$$

Hydriodate of Diæthylamarine, $C^{42}H^{16}(C^4H^5)^2N^2,IH$, is far more readily soluble in water and alcohol than the corresponding salt of amarine. Æther only dissolves traces of it. The alcoholic solution may easily be supersaturated, so that it will long remain clear, and then, when shaken, suddenly deposit crystals. This salt fuses at 392°—410° F. to form an oil, which solidifies at 302°—320° F. into a transparent, amorphous mass. At a higher temperature it is decomposed.

Muriate of Diæthylamarine, $C^{42}H^{16}(C^4H^5)^2N^2,ClH$, is readily soluble in alcohol and in boiling water. The alcoholic solution is not precipitated by water.

The muriate furnishes crystalline precipitates with the bichlorides of platinum and mercury. The platinum double salt is soluble in alcohol, and may be obtained from its alcoholic solution in prisms.

The *sulphate* and *acetate* dry into gum-like masses, when the solutions are evaporated.

If diæthylamarine be treated with potash, when dissolved in alcohol, iodide of potassium and a new base are obtained; the latter may be readily crystallized, when it forms oblique rhombic prisms. It is nearly insoluble in water, but dissolves readily in alcohol; boiling alcohol appears to dissolve it in almost any quantity. Diæthylamarine also dissolves in æther, and crystallizes from this solution. It fuses at 230°—239° F., and solidifies at 158° F. When further heated, it begins to boil and is at the same time decomposed. Concentrated sulphuric and nitric acids attack it.

If diæthylamarine be treated again with iodide of æthyle for some hours at a temperature of 176°—212° F., it furnishes a resinous viscous mass, which is soluble in alcohol and æther, and is very similar to the product obtained in the æthylization of hydrobenzamide.

This body is somewhat soluble in boiling water; the solution becomes milky on cooling, and afterwards clears itself by the aggregation of oil drops. Ammonia produces a white precipitate in this solution. Oxide of silver and oxide of lead form iodides of silver and lead, whilst a new base is produced, which crystallizes in flattened rhombic prisms when the solution is evaporated. It is scarcely soluble in water, but the solution has a strong bitter taste. Æther dissolves it, but only in small quantity. It fuses at about 194° F. When heated upon platinum-foil, it fuses; the products of the decomposition are volatile, and leave no coal. The sulphate resembles that of diæthylamarine. The chloroplatinate crystallizes in small square tabular prisms of an orange-yellow colour.

When this new base is again treated with iodide of æthyle at 212° F., it undergoes a further change, so that amarine must contain at least 3 atoms of hydrogen displaceable by radicals, still belonging to the ammonia type. The groups of hydrogen and

carbon, which replace the residue of the hydrogen of the ammonia, must consequently contain less hydrogen than the group $C^{14}H^6$; amarine and hydrobenzamide have therefore the same molecular constitution. Amarine may be regarded as 1 molecule of ammonia in which 1 equiv. of hydrogen has been replaced by ammonium, for it only saturates 1 atom of acid, whilst it nevertheless contains 2 equivs. of nitrogen. Its formula is perhaps

$$N\left\{\begin{matrix}(C^{14}H^5)^3, H\\ H\\ H\end{matrix}\right. .$$

Bull. de St. Pétersb. xvii. p. 38.

On Seleniuret of Sodium and Antimony. By G. Hofacker.

The author has prepared the selenium compound, analogous to Schlippe's salt.

In the first place he prepared seleniuret of antimony, $SbSe^3$, by fusing together equal parts of selenium and antimony in a porcelain crucible; it is obtained in lead-gray lumps with a jagged fracture, and exactly of the aspect of gray antimony ore.

3 equivs. of anhydrous carbonate of soda were then fused with 1 equiv. of seleniuret of antimony, 3 equivs. of selenium, and the corresponding quantity of charcoal powder, in a Hessian crucible, which was completely luted with the exception of a small opening; the mass was kept in a fluid state at a moderate heat for half an hour, poured out, powdered, and boiled, after 2 more equivs. of selenium had been added, with previously boiled water.

The solution contains the seleniuret of sodium and antimony, which, however, is not easily obtained in crystals by concentrating the solution; during this process the air must be excluded. It is, however, precipitated by alcohol from the aqueous solution, and when the latter is covered with a stratum of alcohol, it may even be obtained in large crystals.

Seleniuret of Sodium and Antimony, $3NaSe + SbSe^5 + 18HO$, is exactly analogous to Schlippe's salt, sulphuret of sodium and antimony, in its composition; it is also isomorphous therewith, tetrahedral faces predominating. It forms orange-yellow, transparent crystals, which become hyacinthine red in the air, and soon become covered with a gray crystalline powder.

The crystals are insoluble in alcohol, and require about 2 parts of water at 53°·6 F. for their solution. When carefully heated in the air, the crystals melt in their water of crystallization, become brown, then gray, and finally break up into a voluminous powder, whilst selenium is volatilized.

The solution of this salt, when long exposed to the air, deposits a gray, laminar powder. The fluid becomes clear and colourless, and contains selenite of soda.

When acids are added in order to dissolve the preceding salt, they precipitate brown perseleniuret of antimony together with red sele-

nium, the latter produced by the oxidation of the seleniuretted hydrogen first evolved. If seleniuret of sodium and antimony be dissolved in boiled water and mixed with muriatic acid, the air being excluded, seleniuretted hydrogen is evolved, and

Perseleniuret of Antimony, $SbSe^5$, is precipitated in the form of a brown powder, which, when heated, loses selenium, and becomes gray and crystalline.

It is reduced with great difficulty in a current of hydrogen. The seleniuretted hydrogen formed is conducted into solution of ammonia.

It dissolves in solution of potash.

The author has also prepared a similar salt containing sulphur and selenium. He first prepared sulphuret of antimony and sodium, $3NaS + SbS^3$, and boiled this with 2 equivs. of selenium without access of air. From this solution alcohol precipitates a yellow salt of the composition $3NaS, SbS^3, Se^2 + 18HO$.

This salt has the same crystalline form as the preceding seleniuret. Sulphur and selenium may consequently replace each other isomorphically in these salts also.—Liebig's *Annalen*, cvii. p. 11.

ANALYTICAL CHEMISTRY.

On a peculiar Case in which Baryta is not precipitated by Sulphuric Acid. By T. Scheerer.

The author observed that in the salt of phosphorus employed in blowpipe experiments, which often contains sulphuric acid, the latter cannot be detected by salts of baryta when the salt has been fused. From this he concluded that metaphosphoric acid prevents the precipitation of sulphuric acid in the form of sulphate of baryta, and further experiments have confirmed this view.

If a large quantity of dilute muriatic acid be added to a solution of metaphosphate of soda, and then solution of chloride of barium, dropped in and mixed by stirring in order that the precipitate of metaphosphate of baryta formed at first may dissolve again in a sufficient excess of muriatic acid and water, the addition of very dilute sulphuric acid to the perfectly clear solution produces no precipitate of sulphate of baryta. After standing for several hours, and sometimes even for days, the fluid begins to grow turbid; but if it be boiled, this operation causes the formation of more or less of a white precipitate.

Repeated experiments showed the author, that the production of these phænomena depends on the degree of dilution of the sulphuric acid, and also that neither the ordinary tribasic phosphoric acid, nor pyrophosphoric acid, has any influence upon the appearance or non-appearance of the sulphate of baryta. At the author's request Dr. Rube then made some further experiments, especially upon the degrees of dilution at which the precipitate makes its appearance.

The solutions employed for this purpose possessed the following degrees of concentration. cc. indicates a cubic centimetre.

A. Solution of metaphosphate of soda in 100 cc.	B. Dilute muriatic acid in 100 cc.	C. Solution of chloride of barium in 100 cc.	D. Dilute sulphuric acid in 100 cc.
In the First Series of Experiments.			
10 gr. $(NaO), aPO^5$.	8 cc. concentrated muriatic acid.	10·50 gr. $BaCl^2$	6·32 gr. SO^3, HO
In the Second Series of Experiments.			
The same.	The same.	19·96 gr. $BaCl^2$	26·94 gr. SO^3, HO.

The results of these experiments were as follows:—

First Series.

Experiment.	Quantity of solutions employed. A. cc.	B. cc.	C. cc.	D. cc.	Precipitate of $BaO\,SO^3$, which should have been produced. grm.	Precipitate produced in 24 hours. grm.	Precipitate produced in 24 hours. grm.
1.	10	300	2·5	2·5	0·295	Traces of turbidity.	Stronger turbidity.
2.	10	300	5	5	0·589	0·038	0·175
3.	15	300	5	5	0·589	0·146	0·337
4.	5	300	5	5	0·589	0·269	0·482

From the comparison of the experiment 2 with 4 and 3, it appears that the quantity of the precipitate increases not only when that of the phosphate of soda is diminished, but also when this is increased. Nevertheless all these precipitates have a different chemical composition, and the quantities of baryta contained in them do not stand in the same proportions as the weights of the precipitates. The turbidities produced in experiment 1, were too small to allow them to be determined quantitatively with accuracy.

Second Series of Experiments.

Experiment.	Quantity of solutions employed. A. cc.	B. cc.	C. cc.	D. cc.	Precipitate of $BaO\,SO^3$, which should have been produced. grm.	Precipitate produced in 24 hours. grm.
5.	20	300	5	5	1·119	0·976
6.	25	300	5	5	1·119	0·622
7.	30	300	5	20	1·119	0·781

The precipitates consisted not only of sulphate, but also of phosphate of baryta; the quantity of phosphoric acid varied from 6—14 per cent.

Dr. Rube also found that strontia and lime behave in an exactly similar way towards metaphosphoric acid. In the presence of metaphosphate of soda also, lime and strontia are not completely precipitated on the addition of carbonate of ammonia.—*Journ. für Prakt. Chemie*, lxxv. p. 115.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Preparation of some Pure Sulphates, and particularly of Sulphate of Copper. *By* HENRY WURTZ, *Prof. Chem., Washington.*

COMMERCIAL *blue vitriol* always contains sulphate of protoxide of iron, which cannot be separated by crystallization, owing to the fact, determined by Mitscherlich, that ferrous sulphate, when cry-

stallizing with sulphate of copper, assumes the pentahydrated composition and triclinic form of the latter, and forms with it homogeneous crystals. It has appeared to me desirable, therefore, that some special method be devised for the separation of the iron, both in order that the chemist may possess a source of pure compounds of copper, and because the presence of iron must be injurious in those processes of dyeing, calico-printing, &c., in which blue vitriol is used, and in the preparation of the cupriferous pigments, *verdigris*, *Paris green*, &c.

In undertaking this, my aim has been to produce a method by which the iron may be directly separated or abstracted from the solution without the permanent introduction of any foreign substance. My process consists essentially of two steps, the first of which is the conversion of the ferrous into *ferric* sulphate, by boiling with a little *deutoxide of lead*, and the second is the *complete* precipitation of the ferric sulphate, by boiling with a little *carbonate of baryta*. The hot solution is then filtered and allowed to crystallize, when large crystals of beautiful form and colour are obtained, containing no trace of iron. Deutoxide of lead is prepared for this purpose by boiling *minium* with dilute nitric or acetic acid in the usual way, but minium itself, if free from soluble impurities, may be used directly in ordinary cases, although a portion of the oxide of copper also is thereby precipitated. *Deutoxide of barium* is of course also applicable.

In cases where the presence of a little *lime* in the product is of no moment, as for the use of the calico-printer and manufacturer of pigments, carbonate of lime may be substituted for that of baryta.

In addition, it may be remarked that if the blue vitriol contains traces of *manganese*, as is extremely liable to occur, this contamination, as would appear from the observations of Schönbein and Wolcott Gibbs, must also be entirely removed.

The same treatment is evidently applicable to some other sulphates, and I therefore present it as a general method for the removal of iron from the sulphates of bases precipitated with difficulty by carbonate of baryta, namely, those of the *alkalies*, *magnesia*, *manganese*, *zinc*, *cadmium*, *mercury*, *nickel*, *cobalt*, and *protoxide of iron*. Of these the most important one practically is the sulphate of magnesia. The mode of proceeding with this would be precisely similar to that with the copper-salt, as it would be also with the sulphates of zinc, cadmium, mercury, nickel, and the alkalies. With regard to the manganous sulphate, it must be remembered that deutoxide of lead, as observed by Schönbein, wholly precipitates sulphate of manganese from its boiling solution; so that the deutoxide must be used only in small excess over the necessary quantity. The same precaution applies, in a modified manner, to the treatment of the cobaltous sulphate, because Gibbs states that the salts of this metal are also partially precipitated by long boiling with an excess of the deutoxide, passing first to a higher state of oxidation.

As to the protosulphate of iron, I have already recommended the use of carbonate of baryta for the removal from it of sesquioxide of iron. In the same paper I have given, among other observations upon the purification of copperas, another method of obtaining its

solution free from ferric sulphate, namely, by acidulation with sulphuric acid and agitation with a little pulverized *protosulphide of iron*, by which the sesquioxide is immediately reduced to protoxide.

To return again to the sulphate of magnesia, before leaving the subject, I must add that the treatment with carbonate of baryta, according to a former observation of my own, must remove also entirely the *sulphate of lime* which usually contaminates commercial Epsom salts; for, as I have there stated, carbonate of baryta totally precipitates gypsum from its solution, even in the cold; and I have there proposed it as a means of removing the gypsum from spring or sea-water which is to be used in steam-boilers (thus preventing *incrustations*), as well as from the brine of salt-works. I have since found that *carbonate of lead* has the same power of precipitating gypsum, and may possibly be a *cheaper* agent for the purpose than carbonate of baryta, considering the facility with which the lead may be *recovered* from the resulting mixture of sulphate of lead and carbonate of lime, in a metallic form*.—Silliman's *Amer. Journ.*, Nov. 1858.

* Although not wholly relevant to the subject of this paper, I may be pardoned a few additional remarks upon this subject of the removal of gypsum from waters. When we call to mind that the *crystallization* of the gypsum from its hot solution is the *principal*, and usually the *only* cause of the formation of the destructive boiler-crusts, and that, leaving out of view the injury sustained by the boiler, the actual *loss of heat* through the non-conducting power of the crust and other causes connected with it, has been shown to amount, in the case of *locomotive boilers* (in France), in many cases to 40 per cent. of the fuel consumed, the subject may be considered worthy of further attention; and I shall therefore present some brief *calculations* bearing upon it.

In a saturated solution of gypsum, then (say, in round numbers, 1 part in 400), each 800 lbs. = 800 pints = 100 gallons will contain 2 lbs., and each 1000 gallons 20 lbs. of sulphate of lime; which is equivalent to 24 lbs. of pure carbonate of baryta, or a little over 31 lbs. of pure carbonate of lead. But water used for steam-purposes, sea-water for instance, is seldom or never a *saturated* solution of gypsum. Let us take von Bibra's analyses of the waters of the Atlantic Ocean (Liebig und Kopp's Jahresber. für 1850, p. 621), collected at four different times, at as many widely distant places. These give in 100 parts 0·205, 0·156, 0·16, and 0·19 parts of sulphate of lime. For the sake of simplicity, take 0·2: then 1000 gallons = 8000 lbs. contain 16 lbs. of gypsum. The quantity of carbonate of baryta equivalent to this is 19·2 lbs., and of carbonate of lead 25 lbs. Thus one ton (2000 lbs.) of carbonate of baryta, which some years since sold in England (in the form of ground *Witherite*) for 20 dollars, is theoretically sufficient to separate the gypsum from 100,000 gallons of the water of the Atlantic. On referring now to the evaporative powers of different coals, as determined by Walter R. Johnson, for the United States Navy Department (Taylor's 'Statistics of Coal,' Introduction, p. lvii; Knapp's 'Chem. Technology,' Am. Ed., i. p. 43), we there find that 1 lb., for instance, of Lackawanna anthracite (considered in New York superior for steam purposes) produces $8\frac{1}{2}$ lbs. of steam from cold water; so that to evaporate 100,000 gallons would require $\frac{8 \times 100{,}000}{8\frac{1}{2}} = 94{,}000$ lbs., or 47 tons. 40 per cent. of such a quantity is over 18 tons.

I do not, however, by any means recommend the application of this principle to *Ocean steamers*, on account of *practical* difficulties, which I see no way to overcome. But *on land* the application is a matter of perfect simplicity. It is only necessary to have the *tanks* from which the boiler is supplied, larger, and to have more of them. While the process of mixture and agitation with the carbonate, and precipitation by standing, is going on in one tank, water may be used from another which has undergone the process. The idea seems to me to be especially applicable to *locomotives*, for which even sea-water may then be used.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Yellow Colouring Matter and the Tannic Acid in Thuja occidentalis. *By* M. KAWALIER.

THE following investigation, recently communicated by Dr. Rochleder to the Vienna Academy, was made by Kawalier in his laboratory.

The fronds of *Thuja*, reduced to small fragments, are boiled with alcohol, and the decoction strained from the undissolved material through linen. On cooling, much wax is deposited from the decoction, and collected on a filter. The filtered fluid is distilled in the water-bath, and the residue mixed with more water, by which means resin and wax are separated. The turbid fluid stops the pores of the filter, so that it cannot be filtered. It is therefore mixed with a few drops of solution of acetate of lead. The suspended impurities are carried down by the small quantity of precipitate produced, so that the fluid may be easily filtered. The filtrate is of a brownish-yellow colour and clear; when mixed with neutral acetate of lead it gives a yellow precipitate, which is collected upon a filter, and washed with water. It is then dissolved in dilute acetic acid; the solution is filtered from any undissolved portion, and the filtrate precipitated with basic acetate of lead. The beautiful yellow precipitate is washed with water, first by decantation, then upon a filter, and then suspended in water and decomposed by a current of sulphuretted hydrogen. The fluid is heated to boiling together with the sulphuret of lead, and filtered upon a water-bath funnel. The sulphuret of lead is washed with a little hot water. The filtrates are heated in a current of carbonic acid until the sulphuretted hydrogen is expelled, and then placed in capsules over sulphuric acid under the bell of the air-pump. After standing for several days, a yellow, crystallized substance separates. The crystals are collected upon a filter, and dissolved in boiling water, to which small quantities of strong alcohol are added until the solution

is effected. By partial evaporation of the fluid *in vacuo* over sulphuric acid the crystals are again deposited; they adhere firmly to the walls of the vessel, and possess a strong lustre and a pure citron-yellow colour. Two recrystallizations are often sufficient to purify them, but sometimes further repetitions of the process are necessary. A solution of the crystals in aqueous alcohol did not acquire a green colour when mixed with a little ammonia. A portion of this citron-yellow body may also be extracted by hot alcohol from the sulphuret of lead washed with water. The taste of the substance is astringent. Under a magnifying power of 380 diameters, the crystals appear to be four-sided prisms. When rapidly heated on platinum-foil, they burn and leave a voluminous coal, which burns away slowly without any ash. Analysis:—

C	52·79	52·82	52·63	52·85	52·88	40	=240	52·86
H	4·94	5·06	5·01	5·15	5·06	22	22	4·84
O	42·27	42·12	42·36	42·00	42·06	24	192	42·30

The author gives this body the name of *thujine*. It has the following properties:—

An alcoholic solution is coloured dark green by a solution of perchloride of iron. Potash and ammonia produce a yellow coloration; the fluid, when exposed to the air, becomes brownish red. Perchloride of tin produces an intense yellow colour, but gives rise to no precipitate. Both acetate and basic acetate of lead produce beautiful yellow precipitates of the colour of chromate of lead; nitrate of silver produces no change, but on the addition of a little ammonia, a grayish black precipitate is thrown down. Sulphate of copper and perchloride of platinum produce no coloration or precipitate. By muriatic and sulphuric acid likewise the fluid is only rendered slightly yellower. Baryta-water at first produces a turbidity, and then a green precipitate, which dissolves readily in water and becomes further changed when the solution is boiled, so that the fluid acquires a reddish-brown colour.

If an alcoholic solution of thujine be mixed with dilute sulphuric or muriatic acid, after it has been heated in the water-bath, it acquires a transitory green colour, but in the next moment again becomes yellow. When it is long heated in the water-bath, a yellow substance separates in proportion as the alcohol is evaporated, so that at last the fluid appears quite colourless. The yellow product of decomposition is indeed nearly insoluble in water, but is soluble in aqueous alcohol, and also in alcohol and æther. The fluid contains sugar, which remains in the form of an amorphous sweet mass, after the removal of the sulphuric acid by carbonate of baryta and the evaporation of the solution filtered from the sulphate and carbonate of baryta. When dried at 212° F., it furnishes a colourless mass, which, after cooling, may be triturated into a white powder. The syrupous solution does not crystallize, even after standing for months. Analysis gave the composition of grape-sugar from which this sugar is distinguished by its incapability of crystallizing. It reduces as much peroxide of copper as grape-sugar from Fehling's fluid.

The quantity of sugar, and that of the yellow product of decomposition, were determined. 100 parts of thujine produced 40·484 per cent. of sugar ($=C^{12}H^{12}O^{12}$), and 66·783 per cent. of the yellow product, which has received the name of thujetine. The two products of decomposition produced from 100 parts of thujine, weighed 107·267. There was consequently a reception of the elements of water; the amount found was 7·3 per cent. on the weight of the substance. The analysis of thujetine dried *in vacuo* at 212° F. gave—

C	54·02	54·25	54·34	28	168	54·19
H	4·41	4·28	4·29	14	14	4·52
O	41·57	41·47	41·37	16	128	41·29

The substance employed in each analysis was prepared separately. The deficiency of hydrogen found is due to the action of the oxygen of the air upon this body in its preparation, as will be seen hereafter.

From the found quantity of the products of decomposition, the splitting of thujine into sugar and thujetine by the assimilation of water takes place in accordance with the following equation:—

$$C^{40}H^{22}O^{24}+4HO=C^{12}H^{12}O^{12}+C^{28}H^{14}O^{16}.$$

According to this 100 parts of thujine should furnish 39·64 of sugar and 68·28 of thujetine (found 40·48 sugar, and 66·78 thujetine), by the reception of 7·9 water (found 7·3).

A solution of thujetine in alcohol, when mixed with a solution of perchloride of iron, acquires an inky appearance, and in course of time a dark precipitate is deposited. Ammonia, added in small quantity, gives the solution a magnificent bluish-green colour. Potash also produces a green colour. By exposure to the air the colour passes to yellow, and then into reddish brown; acids then throw down a red body. Baryta-water produces a green precipitate which, when boiled, becomes reddish brown. Acetate of lead and basic acetate of lead both furnish red precipitates. The pale red precipitate produced by basic acetate of lead, acquires a fine dark red colour by boiling. Perchloride of tin gives the solution an intense yellow colour, without producing a precipitate. Nitrate of silver immediately renders the fluid blackish gray; a precipitate is subsequently deposited. With perchloride of platinum no change is perceived at first, but the fluid soon becomes yellowish brown. Dilute muriatic and sulphuric acids produce no change, nor do they cause any further decomposition when aided by heat.

Thujetine was boiled with baryta-water; after some time dilute sulphuric acid and then alcohol were added, and the whole, whilst hot, was put upon a filter to separate the sulphate of baryta. The body separated from the baryta was deposited from the filtered fluid in flakes, which appeared under the microscope to be fine acicular crystals. After the cooling of the fluid, the flakes were collected upon a filter, washed with water, dissolved in hot alcohol, and again thrown down by water from the solution. Dried *in vacuo* at

212° F., this substance had the following composition :—

C	59·13	59·20	28=168		59·36
H	4·02	4·03	11	11	3·88
O	36·85	36·77	13	104	36·76

This acid, obtained by the action of baryta upon thujetine, is named *thujetic acid*. Thujetic acid is therefore produced from thujetine by the elimination of hydrogen and oxygen. The preparation and investigation of its salts was necessarily put off, on account of the small quantity of material at the author's command.

Thujetic acid is also produced, together with crystallized sugar, by the decomposition of thujine with baryta-water, with the aid of heat. Thujine was treated with hot baryta-water in an atmosphere of hydrogen gas. After boiling for two hous, the decomposition was complete. The thujine dissolves at first in baryta-water, forming a dark yellow solution. An orange-yellow precipitate is soon afterwards produced, and the colour of this becomes gradually darker as the boiling is continued, until at last it appears dark reddish yellow. After the completion of the decomposition the hydrogen gas is replaced by carbonic acid, a current of which is conducted into the fluid, until all the baryta is converted into carbonate and bicarbonate of baryta and the fluid has become cold. The carbonate of baryta, which is of a yellow colour, is separated by filtration from the fluid, washed with water, and treated with acetic acid, by which means the carbonate of baryta is dissolved, and the thujetic acid remains. It is washed with water, in which it is nearly insoluble, and dissolved in alcohol; the solution is filtered, and the filtrate mixed with water, when the thujetic acid separates of a pure citron-yellow colour. When collected on a filter, and dried at 212° F. *in vacuo*, it showed the following composition :—

C	59·48	28=168		59·36
H	4·22	11	11	3·88
O	36·30	13	104	36·76

The baryta was separated by sulphuric acid from the fluid filtered from the carbonate of baryta and thujetic acid, a few drops of basic acetate of lead were added to the fluid, the filtrate freed from traces of lead by sulphuretted hydrogen, the sulphuret of lead removed by filtration, and the solution evaporated in the water-bath. There remained a sweet residue, of the consistence of honey, which exhibited all the reactions of sugar, and crystallized after standing for a short time. The crystals dried at 212° F., showed the composition of grape-sugar.

C	39·79	12=72		40·00
H	6·88	12	12	6·67
O	53·33	12	96	53·33

Just as thujine is decomposed by muriatic or sulphuric acid, with the aid of heat, into thujetine and an amorphous sugar, so also is it split by the action of baryta and heat into thujetine and a crystal-

lizable sugar; the thujetine is at the same time converted into thujetic acid.

It appears from the composition of thujine that sugar and thujetine, as also sugar and thujetic acid, are produced therefrom by the assimilation of the elements of water. We shall see directly that it is possible to decompose thujine in such a manner, that besides sugar, a substance is produced which contains less hydrogen and oxygen than thujetine, and more than thujetic acid. This body, to which the name of *thujigenine* has been given, is contained ready formed in small quantities in *Thuja occidentalis*.

It was stated above, in describing the preparation of thujine, that the alcoholic decoction of the frond of the *Thuja* is filtered, then the alcohol is got rid of by distillation, the residue mixed with water and afterwards with a few drops of acetate of lead, when a yellow precipitate is produced by acetate of lead. The yellow fluid filtered from this precipitate furnishes another precipitate with basic acetate of lead; this is washed with water, suspended in water, and then decomposed by a current of sulphuretted hydrogen. The fluid was boiled with the sulphuret of lead, and filtered upon a water-bath funnel. The sulphuretted hydrogen was displaced from the fluid by carbonic acid, and the fluid was then placed *in vacuo* over sulphuric acid. When a certain degree of concentration was attained, flakes separated in the fluid. When this body is once separated, it is very difficult of solution in water, so that it may be almost completely precipitated by water from its alcoholic solution. Under the microscope (380 diameters) it is seen to be crystallized in needles, which are soluble in alcohol. The solution, like that of thujetine, acquires a splendid green colour with a tinge of blue, when ammonia is added to it. Thujine is usually contaminated with this thujigenine, and consequently repeated recrystallization is necessary for its preparation in a pure state. When dried *in vacuo* at 212° F., thujigenine gave the following numbers on analysis:—

C	57·74	28	=168	57·53
H	3·85	12	12	4·11
O	38·41	14	112	38·36

The slight excess of carbon and deficiency of hydrogen, show that at a high temperature thujigenine may perhaps have a tendency to pass over into a body, $C^{28}H^{11}O^{13}$, that is to say thujetic acid, or that it may be contaminated with a small amount of the latter.

The production of thujigenine from thujine was exhibited in the following experiment:—An alcoholic decoction of *Thuja* was treated as above described for the preparation of thujine. The fluids obtained by the decomposition of the precipitates produced by solution of acetate of lead, and afterwards by basic acetate of lead, were evaporated *in vacuo* over sulphuric acid, until thujine and thujetine began to separate. These small quantities were removed by a filter, and the fluids were mixed with muriatic acid, and heated in the water-bath. As soon as a turbidity was perceptible, the fluid was removed from the water-bath, and rapidly cooled by surrounding

the capsule with cold water. The body which separates during this refrigeration is thujigenine. It was collected on a filter, dissolved in alcohol, and precipitated from this solution by the addition of water. When dried at 212° F. *in vacuo* its analysis gave—

C	57·73	28	168	57·53
H	3·92	12	12	4·11
O	38·35	14	112	38·36

In this case also a small intermixture of $C^{28}H^{11}O^{13}$ is indicated by the excess of carbon and deficiency of hydrogen. By further heating the fluid from which thujigenine has been deposited, and then cooling it again, thujetine is obtained contaminated with a red body, which may be got rid of by repeated solution in alcohol and precipitation by water, when the thujetine is obtained in a pure state.

From this it is clear that the splitting of thujine under these circumstances takes place in accordance with the equation—

$$C^{40}H^{22}O^{24} + 2HO = C^{12}H^{12}O^{12} + C^{28}H^{12}O^{14}.$$

Thujine. Sugar. Thujigenine.

Chloride of acetyle ($=C^4H^3O^2Cl$) was poured over thujigenine in a small flask, which was united to a refrigeratory apparatus, directed upwards, in such a manner that any chloride volatilized on the application of heat, must flow back. After the action had been continued for a quarter of an hour at a boiling heat, the chloride of acetyle was distilled off. By the action of the chloride, the thujigenine immediately acquired an orange-red colour. After the chloride of acetyle was distilled off, alcohol was poured over the residue, which is soluble in that fluid. This solution deposits no crystals on the addition of water, but lets fall a resinous mass, which contracts into a lump. The solution of this body in alcohol very soon acquires a reddish tinge when exposed to the air; after its evaporation in a capsule on the water-bath, it leaves a reddish-yellow residue, when the alcohol evaporated has been replaced by water. This body is thujigenine, in which 1 equiv. hydrogen is replaced by acetyle ($=C^4H^3O^2$). The substance dried *in vacuo* at 212° F. gave the following numbers on analysis:—

C	57·15	32	192	57·48
H	4·01	14	14	4·19
O	38·84	16	128	38·33

Thujigenine is homologous with the aloine obtained from Barbadoes aloes. Aloine dried at 212° F. has a composition corresponding with the formula $C^{34}H^{18}O^{14}$. But $C^{34}H^{18}O^{14}$ is $C^{28}H^{12}O^{14} + C^6H^6$. The properties of the two bodies appear also to be in favour of this connexion.

[To be continued.]

Investigation of Veratric Acid. *By* W. Merck.

In preparing veratrine from Sabadilla seeds the author obtained a small quantity of this acid, and it appeared to him that a further

investigation of it would not be without interest. In its preparation he adopted the method described by his father (Liebig's Annalen, xxix. p. 188), but only obtained 40 grms. of pure acid from 5 cwts. of the seeds, a small result, probably caused by the ready decomposability of the acid.

To convince himself of the purity of his acid he analysed it, and obtained numbers exactly agreeing with the formula $C^{18}H^{10}O^{8}$, established by Schrötter for veratric acid.

	Found.	Calculated from Schrötter's formula.	
C	58·74	C^{18}	59·34
H	5·62	H^{10}	5·49
O	35·64	O^{8}	35·17

The analysis of the silver-salt gave 37·76, 37·59, and 37·81 per cent. of metallic silver; the formula requires 37·76 per cent.

The following are the results obtained by the author by treating veratric acid with various reagents. When this acid is brought in contact with strong nitric acid, it dissolves with a violent evolution of heat, and on the addition of water, a yellow body, nitroveratric acid, is separated. This acid is but sparingly soluble in water, dissolves very readily in alcohol, and is obtained from the latter in small yellow crystalline laminæ. When heated above 212° F. it is decomposed. The analysis of nitroveratric acid gave—

	Found.			Calculated.
C	47·14	47·34	47·43	47·57
H	4·68	4·50	4·42	3·96
N	..	..	6·78	6·16
O	..	..	41·37	42·31

These numbers correspond with the formula $C^{18}H^{9}NO^{12}$.

If nitroveratric acid be again boiled with concentrated nitric acid, the binitro-compound is easily obtained; this crystallizes from the alcoholic solution in needles of a faint yellow colour, and is essentially different from the above-described nitro-compound. It is difficult to separate from the mononitroveratric acid, so that no exact analysis of it could be obtained.

Chlorine and bromine act very energetically upon veratric acid; hydrochloric and hydrobromic acids are evolved, and the corresponding products of substitution are obtained. From their resinous nature, however, these are not fitted for further investigation.

Perchloride of phosphorus has no action upon veratric acid.

If veratric acid be mixed with three times its weight of baryta, and gently heated in a retort, a brisk reaction takes place, and a colourless oleaginous body distils over. The mixture must be very gradually heated at first, for when the heat is too quickly applied, the mass readily ignites, causing considerable loss.

The body thus obtained, for which the author proposes the name of *veratrole*, possesses a pleasant aromatic odour, has a spec. grav. of 1·086 at 59° F., boils between 396° and 401° F., and solidifies at

59° F., forming a crystalline mass. It is not acted upon by alkalies and weak acids. Its analysis gave—

	Found.	Calculated.
C	69·49	69·56
H	7·70	7·24
O	22·81	23·20

These numbers agree with the formula $C^{16} H^{10} O^4$. Veratric acid therefore loses 2 equivs. of carbonic acid by distillation with baryta.

Fuming nitric acid acts very energetically upon veratrole. Mononitroveratrole is first obtained; it crystallizes from the alcoholic solution in yellow laminæ. By longer action of the nitric acid, binitroveratrole is produced. The latter crystallizes in long yellow needles, and dissolves with difficulty in water, but readily in alcohol. When heated above 212° F., it fuses and becomes volatilized, and at the same time decomposed. The analysis of binitroveratrole gave—

	Found.			Calculated.
C	41·22	42·31	42·22	42·10
H	3·46	4·02	3·96	3·50
N	..	..	11·69	12·28
O	..	..	42·13	42·12

corresponding with the formula $C^{16} H^8 N^2 O^{12}$.

Veratrole is very violently attacked by bromine; hydrobromic acid is evolved, and a crystalline mass is obtained, from which the bibromide may be easily prepared by repeated recrystallization. Bibromoveratrole is insoluble in water, but dissolves readily in æther and alcohol, and separates from the latter in white prismatic crystals. It fuses at 198° F., and is volatile at a higher temperature without decomposition. Its analysis gave 54·17 per cent. of bromine; the formula $C^{16} H^8 Br^2 O^4$ requires 54·04 per cent. By the long action of bromine upon veratrole, products of substitution still richer in bromine are formed; these, however, are not crystallizable.

Chlorine acts upon veratrole exactly in the same way as bromine; a white crystalline mass is first obtained, and this is converted into a slimy product by the long-continued passage of chlorine. The analysis of the chlorine compound was not effected from want of material.

To ascertain in what class of bodies veratrole belongs, the author made some experiments with a small quantity, but obtained only negative results. Neither perchloride of phosphorus nor hydrochloric acid act upon veratrole; potassium certainly converts it into a gelatinous mass, but no evolution of hydrogen can be observed at the same time. Bisulphite of soda and nitrate of silver likewise appear to have no action upon it.—Liebig's *Annalen*, Oct. 1858, p. 58.

On Spanish Zinc-bloom. By T. Petersen *and* E. Voit.

The hydrated carbonate of zinc (zinc-bloom) of the Spanish zinc deposits appears to possess no definite composition, as the analyses of different samples of ore exhibit considerable variations.

Smithson gives the formula

$$3ZnO\,CO^2+3HO$$

for zinc-bloom.

The zinc-bloom from Santander investigated by the authors forms compact, homogeneous masses with a splintery fracture and a pure white colour, frequently with angular partings, the interstices of which are penetrated by siliceous oxide of zinc and calamine. Its spec. grav. was found to be 3·252.

The first analyses (A.) were made with fragments from the interior of large pieces. Three months afterwards the broken pieces were again examined and found to be rather different in composition (B.). In course of time, they imperceptibly underwent a further change. The zinc-bloom* also soon lost carbonic acid and water when gently heated.

Analyses A.

	I.	II.	III.	IV.	V.	Average.
ZnO	73·0	73·12	73·14	..	..	73·1
CO^2	..	14·8	..	15·1	15·3	15·1
HO	..	11·88	..	..	..	11·8

Analyses B.

	I.	II.	III.	IV.	V.
ZnO	74·15	74·33	74·82	74·58	74·73
CO^2	..	..	..	..	13·81
HO	..	..	..	..	11·45

Zinc-bloom is almost completely soluble in a mixture of ammonia and carbonate of ammonia. 0·549 grm. left only 0·003 grm. of insoluble residue containing zinc; it contained siliceous galmei and traces of oxide of iron and lime.

The analyses A. agree with the precipitate ($8ZnO, 3CO^2, 6HO$) constantly obtained by Lefort by the precipitation of equal equivalents of a salt of zinc and carbonate of soda at a boiling heat; the analyses B., on the contrary, may be reduced to the formula ZnO, CO^2+2ZnO, HO. The composition of the siliceous oxide of zinc also is not unfrequently different even in pure crystallized fragments of similar appearance.—Liebig's *Annalen*, Oct. 1858, p. 48.

On the Action of Ammonia upon Chlorobenzole.

By A. Engelhardt.

The author's previous investigations led him (like Limpricht) to the opinion that chlorobenzole is the perchloride of the biatomic alcoholic radical $C^{14}H^6$, as, by its action upon silver-salts, æthers of the biatomic alcohol, $C^{14}H^8O^4$, are produced. Thus, for example,

* In a letter to Prof. Weltzien, M. Braun gives two analyses of the same zinc-bloom. These nearly approach those of the authors.

	I.	II.
ZnO	73·15	73·83
CO^2	13·33	14·32
HO	12·96	11·87
Intermixed silicate of zinc	1·34	

the composition of the neutral æther which is produced, with separation of chloride of silver, by the action of chlorobenzole upon benzoate of silver, may be expressed by the formula

$$\left.\begin{matrix}(C^{14}H^{5}O^{2})^{2}\\ C^{14}H^{6}\end{matrix}\right\}O^{4}.$$

It now occurred to him to ascertain the behaviour of chlorobenzole towards ammonia, and especially whether amide-compounds of the biatomic alcohol $C^{14}H^{8}O^{4}$ would be obtained. The first experiments made by the author for this purpose with aqueous ammonia and chlorobenzole, produced no result. Buff also, who employed alcohol saturated with ammonia, obtained no favourable result, as was also the case with Wicke, who investigated the action of dry ammoniacal gas upon chlorobenzole. By heating a mixture of aqueous ammonia and chlorobenzole to 212° F. in a sealed tube, Wicke only obtained oil of bitter almonds and chloride of ammonium.

Further experiments, however, showed that the desired object might be attained by the action of aqueous ammonia upon chlorobenzole, when this was longer continued. The crystalline compound thus obtained is identical with the hydrobenzamide previously prepared from oil of bitter almonds and ammonia.

Chlorobenzole was treated with about twenty volumes of liquid ammonia and kept in a well-closed bottle for several months at the ordinary temperature. The aqueous fluid, which still smelt strongly of ammonia, was poured away from the lower stratum and carefully evaporated to dryness, when the residue proved to be chloride of ammonium. The crystalline mass obtained by the action of ammonia upon chlorobenzole was separated from the supernatant, oleaginous, reddish-brown substance, pressed between bibulous paper, washed with a little æther, and dissolved in cold æther. When the æther was slowly evaporated, transparent crystals separated; these exhibited the same appearance as the crystals of hydrobenzamide described by Laurent. By the action of muriatic acid they are decomposed into oil of bitter almonds and chloride of ammonium.

They also possessed all the properties of hydrobenzamide. It is clear therefore that hydrobenzamide and chloride of ammonium are formed by the action of ammonia upon chlorobenzole,—

$$3\,C^{14}H^{6}Cl^{2}+8\,NH^{3}=N^{2}(C^{14}H^{6})^{3}+6\,NH^{4}Cl.$$

Chlorobenzole. Hydrobenzamide.

Bull. de St. Pétersb., xvii. p. 168.

On the Nitrates of Iron. *By* A. Scheurer-Kestner.

The author's investigations establish the following facts:—

1. Whilst an acid of spec. grav. 1·034 only produces protonitrate of iron and ammonia with iron, an acid of 1·073 furnishes a mixture of proto- and pernitrates of iron and nitrate of ammonia, and one of 1·115 only produces pernitrate of iron and no ammonia.

2. With an acid above spec. grav. 1·115 only pernitrate of iron is

obtained. But this is not pure neutral nitrate; it is a mixture of neutral nitrate with several different basic nitrates.

3. The quantity of basic salts formed, and the heat evolved during the reaction, are nearly in a direct ratio to the concentration of the acid employed. The concentration of the liquids also influences the formation of basic salts.

4. The neutral nitrate

$$Fe^2O^3, 3NO^5, 18HO$$

alone crystallizes; the sesquibasic and tribasic salts are uncrystallizable, and their presence hinders the crystallization of the neutral nitrate.

5. The neutral nitrate is not precipitated from its aqueous solution by nitric acid, which simply decolorizes it.

6. Ebullition with water decomposes all the three salts above mentioned.

The neutral nitrate by decomposition furnishes a salt of which the formula is

$$2Fe^2O^3, NO^5, HO,$$

a formula which may be thus interpreted—

$$Fe^2O^3, NO^5, Fe^2O^3, HO.$$

The sesquibasic nitrate gives a body the formula of which is

$$3Fe^2O^3, NO^5, 2HO = Fe^2O^3\,NO^5, 2(Fe^2O^3, HO).$$

The tribasic nitrate furnishes a body with the formula

$$4Fe^2O^3, NO^5, 3HO = Fe^2O^3, NO^5, 3(Fe^2O^3, HO).$$

The series of pernitrates of iron therefore contains the following terms:—

$Fe^2O^3, 3NO^5$.....	Neutral nitrate.
$Fe^2O^3, 2NO^5$.....	Sesquibasic nitrate.
Fe^2O^3, NO^5	Tribasic nitrate.
$2Fe^2O^3, NO^5, HO$ ..	Produced from the neutral nitrate.
$3Fe^2O^3, NO^5, 2HO$..	Produced from the sesquibasic nitrate.
$4Fe^2O^3, NO^5, 3HO$..	Produced from the tribasic nitrate.

Comptes Rendus, Dec. 6, 1858, p. 927.

Note on the Coloration of the Salts of Manganese, and on Oxalate of Manganese. *By* A. Gorgeu.

The fact which constitutes the principal subject of this note is the existence of two crystallized oxalates of manganese of different colours, one *rose-coloured*, the other *colourless*.

The rose-coloured salt is prepared in the form of beautiful prismatic needles by pouring a cold solution of oxalic acid into an excess of a cold solution of pure sulphate of manganese. The white salt is more difficult to obtain in a crystalline form; a hot solution of oxalic acid must be poured gradually into a very hot solution of a pure salt of manganese until a precipitate begins to appear; the

mixture is then left to cool very slowly. In this way the white oxalate is obtained in the form of flattened octahedra.

The author has made several attempts to ascertain whether there exists a series of colourless crystallized salts of manganese; the oxalate just mentioned appears to be the only one fulfilling these conditions.

With the view of ascertaining whether the simultaneous existence of these two oxalates is irreconcileable with the hypothesis of a rose-colour inherent in the salts of manganese, as the clear green colour is in those of protoxide of iron, the author investigated the composition and properties of the two oxalates, and arrived at the following results:—

1. The two oxalates of manganese differ essentially in their chemical composition; that of the rose-coloured oxalate is represented by the formula $C^2O^3\,MnO, 3\,HO$, whilst that of the colourless salt is represented by $C^2O^3\,MnO, 2\,HO$.

2. The two oxalates, although belonging to the same crystalline system, present forms, as ascertained by M. Descloiseaux, which appear to be incompatible.

The affinity of these two bodies for their water of crystallization is different. When exposed to the air, the white salt undergoes no alteration, whilst the rose-coloured salt in time loses an equivalent of water, and becomes transformed into the white salt, $C^2O^3\,MnO, 2\,HO$; *in vacuo*, the white salt does not change in weight, whilst the rose-coloured salt parts with the greater part of its water without losing its transparency and colour; at a temperature of 203° F. the white salt undergoes no alteration, whilst the other evolves $\frac{9}{10}$ths of its water, and still retains a faint rosy tint.

In presence of these results, and if it be admitted that a simple change in the disposition of the molecules or in the state of hydratation of a body may correspond with a change of colour, it does not appear too much to suppose that this effect may be produced in a salt of which the chemical composition, and some of the physical and chemical properties have been modified.

Thus the simultaneous existence of the two oxalates is not essentially opposed to the hypothesis which ascribes a peculiar coloration to the salts of manganese, since the want of colour in the oxalate with 2 HO, may be the result of chemical and physical differences existing between it and the rose-coloured salt.—*Comptes Rendus*, Dec. 6, 1858, p. 929.

On a crystallized Compound of Caseine. *By* O. Maschke.

The author has prepared a crystallized compound of caseine with an organic acid which has not yet been more accurately determined. The crystals of this compound are microscopic, but reflect the light very strongly, so that they may be seen with the naked eye in the sun-light. The slightly alkaline solution of these crystals, when mixed with sugar of milk and rennet, coagulates, like milk, in the course of two days. These crystals were prepared from the Para

nut (the seed of *Berthelotia excelsior*), but may also be prepared from all the other seeds which contain caseine vesicles (Hartig's *Klebermehl-Aleuronkrystalle*).—*Journal für Prakt. Chemie*, lxxiv. p. 436.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Manufacture of the Uchatius Cast Steel.
By THOMAS SPENCER.

CAST STEEL, perhaps, beyond all other available metals, possesses the qualities of strength and durability, and it is only its great cost that has hitherto prevented its more general application in the manufacture of machinery. It has a bearing strength of nearly three times that of the best-forged iron, and having a perfectly uniform texture, it wears equally. It must therefore be acknowledged that cast steel is the best material that can be used where lightness and strength are required, and for all parts of machinery that are subject to much wear and tear. The cost of cast steel being the difficulty in the way of its extended application, the object for some years past has been to produce it at a price that would allow of its free employment. Amongst a great number of metallurgists who have within a very recent period directed their attention to this subject, may be mentioned Bessemer, Chenot, Uchatius, and others. It is intended in this paper to enter only into the details of the Uchatius process of making cast steel, as compared with the ordinary processes at present in extensive use, which are two,—the English or converting process, and the German or puddling process.

To compare these processes with the Uchatius process about to be described, it must first be considered what steel really is, and in what manner it may be produced. This point may be illustrated by the following series, comprising the various degrees of wrought iron, steel, and cast iron, arranged according to the amount of carbon in each, beginning with the softest wrought iron, that is, with the iron containing no carbon, or the least amount of carbon:—

Soft wrought iron,	containing	0·0	per cent.	of carbon.
Hard wrought iron	„	0·4	„	„
Soft steel	„	0·5	„	„
Hard steel	„	2·4	„	„
Cast iron	„	2·5	„	„
Hard cast iron	„	5·9	„	„

In this series, beginning with the softest wrought iron, containing little or no carbon, the proportion of carbon increases until there is $\frac{1}{2}$ per cent., which then forms soft steel; a further increase of carbon up to $2\frac{1}{2}$ per cent., forms cast iron; and the proportion of carbon increasing to 5 per cent., gives the hardest cast iron. Hence it appears that the operation of steel making may be effected in two me-

thods,—either by adding a certain amount of carbon to pure wrought iron, or, conversely, by taking away a certain amount of carbon from cast iron, removing at the same time the impurities of the cast iron.

The English or converting process is carried on according to the first of these methods, by adding a certain amount of carbon to wrought iron. The cast iron is first made into wrought iron, which is then converted into steel, forming blister steel. This is broken into small pieces, and melted in crucibles, which renders it homogeneous, and it is then poured, while fluid, into ingot moulds; after which it is known as cast steel. The chemical changes which the cast iron has undergone in this process are,—first, when it was manufactured into wrought iron, all, or nearly all, the carbon was abstracted from it; and secondly, by the converting process, a certain amount of carbon was restored to it; and, finally, the steel thus produced was made homogeneous by melting and casting. It is evident that this is a very circuitous way of manufacturing cast steel, and it has the following disadvantages: the great loss of weight in manufacturing the cast iron into wrought; the difficulty in converting the wrought iron, so as to carbonize it equally in all parts; the great length of time that this process requires for the production of cast steel; and the great cost of manufacture.

The German or puddling process is effected by the converse method, by taking away a certain amount of carbon from cast iron. The pig-iron is puddled in the same way as in making wrought iron, except that the process is stopped when a certain amount of carbon has been taken away, a point which it is difficult to judge of. This partially puddled iron, or so-called puddled steel, is then made homogeneous by melting it in crucibles, in the ordinary way. The chemical change which the cast iron has undergone by this process is the abstraction of a portion of the carbon in the puddling furnace; and the puddled steel has then been rendered homogeneous by melting and casting. The disadvantages of this method are—the waste of iron by the puddling process; the uncertainty of getting equally decarbonized iron, owing to the difficulty of measuring the quantity of oxygen acting on the puddled metal; and also the cost of manufacture.

The Uchatius process is based upon the same principle as that last described, consisting in taking away as much carbon only as is required to produce steel, and removing at the same time the impurities of the cast iron. The first and most important of these objects is effected by bringing a certain measured quantity of oxygen, in the shape of oxides of iron, in contact with the cast iron, so that while the iron is hot, the oxygen combines with the carbon, and passes off in the form of carbonic acid gas. The purification of the cast iron from silica, sulphur, magnesia, &c., is effected by bringing the iron, when it is in a melted state, into contact with alkaline earths, so that the impurities combine with them, and remain floating on the top of the melted metal.

In order to effect these two operations at the same time, the pig iron iron is first melted in a furnace or ordinary foundry cupola, and then

run into a cold-water tank, where it is reduced into small granules. The granulation is performed by the use of a horizontal wheel, placed in a cold-water tank, and provided with wooden floats, dipping below the surface of the water. While this wheel is driven at a considerable speed, the melted metal, running from the furnace, falls on the wheel, which scatters it in a finely divided state; and the bottom of the tank being inclined downwards from the wheel, it falls to the bottom in the form of small granules. This granulated cast iron is mixed with pulverized oxide of iron and some alkaline earths, and the whole put into the ordinary steel-melting crucibles, and placed in the furnaces, and brought into a fluid state. The degree of hardness of the steel is thus capable of being regulated by the size of the granules and by the quantity of oxides used.

The chemical change which takes place within the crucible is as follows:—Each granule being surrounded by the pulverized oxide, &c., the decarbonization takes place first on the outside of each granule, and so progresses towards the centre as the heat increases; the oxygen in the ores combining with the carbon in the granules and passing off as carbonic acid gas. If, therefore, during the process, the granules could be examined, it would be found that the outside of each is entirely deprived of its carbon, the next portion partially decarbonized, and the centre not decarbonized at all: so that each granule would be composed of pure wrought iron, steel, and cast iron. By increasing the heat, the cast-iron centre portion of the granule first becomes fluid, and the granule bursts and falls by its own weight to the bottom of the crucible; at the same time the earths mixed with the ores melt and rise to the top, forming a layer of scoria or dross floating on the surface of the melted iron. Each granule of melted metal has therefore, in falling, to pass through the rising scoria; and it is in the passing through that the combination of the impurities of the metal with the alkaline earths takes place, so that the decarbonized iron, on reaching the bottom of the crucible, is cleansed from all impurities. The heat, continuing to increase, melts the outside portions of the granules, and the whole is reduced to one homogeneous fluid mass in the crucible, which is then ready for being poured into the ingot moulds. The iron contained in the oxides mixes at the same time with the fluid mass, and yields about 6 per cent. more of cast steel than the weight of granules put into the crucible.

The oxides employed in this process are iron ores of the finest quality, such as spathose and hæmatite, which are previously calcined and pulverized. The proportion of the oxide to the granulated iron is according to the hardness of steel required, say from 20 to 30 per cent.; the greater the quantity of the oxide employed, the greater the decarbonization, and consequently the softer will be the steel produced.

This process is attended with the following advantages:—A rapid manufacture of cast steel, the pig-iron being converted into cast steel in the space of a few hours; certainty in producing a uniform quality of steel, that is steel containing a determinate proportion

of carbon, which is accurately determined beforehand by the weight of oxide mixed with the granulated iron; and less cost than the ordinary methods of making cast steel, since the processes are fewer, and the materials used are simply pig-iron and iron ores.

Some experiments in making cast steel by the Uchatius process, made by the writer at the Newburn Steel Works, near Newcastle-on-Tyne, showed that a very fine quality of cast steel could be produced at a cost little more than one-half of that entailed by the common processes.—From the Proceedings of the Institution of Civil Engineers, as reported in Newton's *London Journal of Arts and Sciences*, February 1859.

On the Sulphuring of Hops. By Professor Siemens.

The author makes the following report upon the sulphuring of hops which is done frequently in Bavaria. The hops are usually sulphured with the view of giving to an old, weak, and ill-looking sample the appearance of being newer and more valuble. An ordinance was lately published in Bavaria, forbidding the employment of sulphured hops in the country, but permitting those intended for exportation to be treated with sulphur. The efficacious constituents of the hop are only contained in sufficient quantity in well-preserved fresh hops; they lose in strength and undergo change when long and imperfectly preserved, and at the same time the hops lose in appearance, especially becoming darker and generally spotted. The ease with which these constituents undergo change, also renders it impossible to replace what is lost by the employment of a larger quantity of hops, so that the quality cannot be replaced by quantity. Consequently, in order to conceal these signs of age, and at the same time the diminished value of the hops, various means have been employed, and amongst these the sulphuring or bleaching of the hops has been found most efficacious.

For this purpose the hops are placed upon a sort of kiln, under which sulphur is burnt, by which means fumes of sulphurous acid are produced, which penetrate the hops and bleach them, so that they acquire the fresher colour of new hops, and when mixed with the latter, may more easily be brought to sale. All hops are not, however, sulphured for this dishonest purpose; the process is also supposed to render them better fitted for long transport, and in England scarcely any but sulphured hops are employed. The beers made in that country are not indebted solely to the addition of hops for their keeping qualities; the aroma of the hops also is lost by the long boiling of those beers.

To those brewers who have to endeavour to prepare, from the smallest possible quantity of malt, a beer which shall have a pleasant, refreshing taste, and of which large quantities may be drunk without intoxicating, it is of the greatest importance to give this beer the necessary keeping qualities and briskness (continued fermentation) by the employment of good new hops. Although therefore sulphured hops are capable of employment where strong

beer is made to be drunk out of wine-glasses, and are even necessary for very pale beer, such as the English ales, because they give a paler beer, such hops are not adapted for those beers which are poorer in alcohol, and less boiled, and which owe their preservability to their protracted fermentation alone.

From this it follows that it is necessary to employ hops containing an abundance of those efficacious constituents, which are only found in new hops. But as the sulphuring of old hops renders it possible to mix them with new hops, and thus sell them as new, it becomes necessary to find some means by which such an adulteration may be detected with certainty.

The practised hop merchant may probably find it not very difficult to distinguish sulphured from new hops, as the difference betrays itself to the practised eye even by the external appearance, but for the unpractised buyer it is always difficult to detect this difference without possibility of mistake.

Amongst these external characters, it is stated that in the sulphured hops the colour of the stalks and leaflets is similar, whilst in unsulphured hops the former are usually darker than the leaflets. The colour of sulphured hops is also much more uniform than that of new hops; but this uniformity ceases when the two kinds are mixed together. The individual leaflets of the heads appear much drier in the sulphured than in fresh hops; this is easily distinguished in mixtures. Moreover, in sulphured hops the other characters of a good sample, its aroma, its fattiness, and the quantity of its yellow pollen, do not bear the proper relation to its externally youthful appearance.

The well-known means of detecting sulphured hops by placing in them a bright piece of silver, which soon becomes of a dark colour, and acquires brown spots in sulphured hops, especially when the sample is heated, can only answer when the operation has been recently performed. Extracting a small portion of the hops with water, and then testing the extract for sulphuric acid by means of a baryta-salt is not certain, because a precipitate is always produced, which, however, usually dissolves again in nitric acid, and such reactions are uncertain in the presence of organic bodies. The precipitate may also be due to water containing sulphate of lime.

The method proposed by Dr. Heidenreich of Ansbach is, however, infallible. A small sample of the hops is treated with distilled or rain-water, and after the lapse of some time the fluid is put into a small glass flask, which may be closely stopped with a cork. The stopper is to be furnished with a bent glass tube, in order to conduct the gas to be evolved in the flask, into a solution of basic acetate of lead. Before the extract of hops is poured in, a small fragment of zinc-foil is put into the flask, and a little pure muriatic acid is added after the pouring in of the extract; the flask is then quickly closed, and the gas conducted into the solution of lead. If the hops were sulphured, the gas evolved will consist more or less of sulphuretted hydrogen, which might be detected, if in large quantity, by its odour, but when in small quantity gives the solution

of lead a dark colour. At first this colour may be recognized even on the bubbles ascending out of the fluid, as when a small quantity of sulphuretted hydrogen is present, they appear as if covered with a brownish film.

Still more remarkable is the reaction of sulphuretted hydrogen, when, instead of solution of lead, the gas is conducted into a dilute solution of nitroprusside of sodium, in which the smallest trace of sulphuretted hydrogen then produces an unmistakeable violet colour, as was first mentioned by Wagner, as an improvement on Heidenreich's method.—*Würtemb. Wochenblatt*, 1858, No. 29.

PROCEEDINGS OF SOCIETIES.

Royal Society.

"On the Action of Nitric Acid and of Binoxide of Manganese and Sulphuric Acid on the Organic Bases." By A. Matthiessen, Ph.D.

In the Proceedings of the Royal Society (vol. ix. p. 118), I stated that by the action of nitrous acid on aniline I had obtained ammonia; since then I have acted upon several organic bases with the same reagent, as well as with nitric acid, and also with binoxide of manganese and sulphuric acid. I will now briefly enumerate these experiments.

I. *Action of Nitrous Acid upon Amylaniline.*—The dilute solution of the nitrate of amylaniline was acted on by nitrous acid at 100° C. for 12 hours. Amylaniline and ammonia were obtained, but in quantities too small for quantitative determination.

II. *Action of Nitric Acid upon Amylaniline.*—Amylaniline was boiled with dilute nitric acid (1 part acid to 2 parts water) until the reaction began, which was immediately stopped by the addition of cold water. The solution was then filtered from the nitrophenasic acid; and after potash had been added, it was again filtered to separate the undecomposed amylaniline. The filtrate was then distilled, the distillate redistilled *per ascensum*, and evaporated to dryness with hydrochloric acid. The residue was finally extracted with absolute alcohol, and the filtrate evaporated to dryness. This operation was repeated four or five times. A platinum-salt made with the chloride, which was soluble in absolute alcohol and recrystallized*, gave 33·55 per cent. platinum. The theoretical quantity required for the chloroplatinate of amylamine is 33·66 per cent. The platinum-salt of that chloride which was insoluble in absolute alcohol gave 43·9 per cent. platinum; the chloroplatinate of ammonium requires 44·2 per cent.

The above reaction may be explained by the following formulæ:—

$$\left.\begin{matrix} C_{12}H_5 \\ C_{10}H_{11} \\ H \end{matrix}\right\} N + \left.\begin{matrix} H \\ H \end{matrix}\right\} O_2 + NO_5HO = C_{12}H_6O_2 + \left.\begin{matrix} C_{10}H_{11} \\ H \\ H \end{matrix}\right\} N + NO_5HO$$

* In each case the platinum-salt was recrystallized from water.

and

$$\left.\begin{matrix} C_{10}H_{11} \\ H \\ H \end{matrix}\right\} N + \left.\begin{matrix} H \\ H \end{matrix}\right\} O_2 + NO_5HO = C_{10}H_{12}O_2 + \left.\begin{matrix} H \\ H \\ H \end{matrix}\right\} N + NO_5HO.$$

The free nitric acid present converts the phenylic alcohol into nitrophenasic acid, and the amylic alcohol into nitrite of amyle.

III. *Action of Nitric Acid upon Ethylaniline.*—Ethylaniline was treated in the same manner as amylaniline. A platinum-salt of the chloride which was soluble in absolute alcohol gave in two experiments,

I. 39·6
II. 39·5 } per cent. platinum.

The chloroplatinate of ethylamine requires 39·3 per cent. The platinum-salt of the chloride insoluble in absolute alcohol gave 44·0 per cent. platinum, which agrees with the number required for the chloroplatinate of ammonium (44·2 per cent.).

IV. *Action of Nitric Acid upon Diethylaniline.*—Diethylaniline was treated with dilute nitric acid (1 part acid to 4 parts water), and heated until the temperature had reached 54° C., when, on being left to itself, it soon became turbid and the temperature rose about 10° C. After a while the solution became clear, but remained very dark. When quite cold, it was filtered from the nitrophenasic acid. The filtrate was now treated in the same manner as described in Experiment II. The solution of the chlorides (5–6 grms. were obtained from about 50 grms. of diethylaniline) soluble in absolute alcohol was partially precipitated with bichloride of platinum (No. 1); then another portion was precipitated, which was not used; after this, more bichloride was added (No. 2), and lastly an excess of the bichloride was added (No. 3).

The platinum found in the three salts was

No. 1.	No. 2.	No. 3.
39·2 per cent.	35·5 per cent.	35·4 per cent.

Chloroplatinate of ethylamine requires 39·3 per cent., and chloroplatinate of diethylamine 35·3 per cent. A platinum-salt made with that chloride which was insoluble in absolute alcohol contained 44·2 per cent. platinum, which is exactly the number required for the chloroplatinate of ammonium.

The reaction was as follows:—

$$\left.\begin{matrix} C_{12}H_5 \\ C_4H_5 \\ C_4H_5 \end{matrix}\right\} N + \left.\begin{matrix} H \\ H \end{matrix}\right\} O_2 + NO_5HO = \left.\begin{matrix} C_4H_5 \\ C_4H_5 \\ H \end{matrix}\right\} N + C_{12}H_6O_2 + NO_5HO;$$

$$\left.\begin{matrix} C_4H_5 \\ C_4H_5 \\ H \end{matrix}\right\} N + \left.\begin{matrix} H \\ H \end{matrix}\right\} O_2 + NO_5HO = \left.\begin{matrix} C_4H_5 \\ H \\ H \end{matrix}\right\} N + C_4H_6O_2 + NO_5HO;$$

and

$$\left.\begin{matrix} C_4H_5 \\ H \\ H \end{matrix}\right\} N + \left.\begin{matrix} H \\ H \end{matrix}\right\} O_2 + NO_5HO = \left.\begin{matrix} H \\ H \\ H \end{matrix}\right\} N + C_4H_6O_2 + NO_5HO.$$

As in the case of amylaniline, the phenylic alcohol and the alcohol

are converted into nitrophenasic acid and nitrite of ethyle, the ammonia being in both cases partially oxidized.

V. *Action of Binoxide of Manganese and Sulphuric Acid on Aniline.*—Aniline was dissolved in an excess of dilute sulphuric acid (1 part of acid to 6 of water) and heated to boiling, when a small quantity of binoxide of manganese was added. The reaction was allowed to continue for 3 or 4 minutes, when it was stopped by cooling the flask in water. Potash was then added and the solution filtered, the filtrate distilled, and the distillate redistilled *per ascensum*. The distillate was evaporated to dryness with hydrochloric acid. The residue was extracted with absolute alcohol, to separate any chloride of aniline which might be present. A platinum-salt of the chloride insoluble in absolute alcohol gave 44·0 per cent. platinum, which corresponds to the platinum of chloroplatinate of ammonium.

VI. *Action of Binoxide of Manganese and Sulphuric Acid.*—Diethylaniline was treated with dilute sulphuric acid and binoxide of manganese, as in Experiment V., the reaction being allowed to last only about one minute. Potash was added, &c., as above described. The solution of those chlorides soluble in absolute alcohol was precipitated as in Experiment IV.; and the platinum found in No. 1 was 37·6, in No. 2, 35·4.

No. 1 is a mixture of the chloroplatinates of ethylamine and diethylamine; the quantity of salt precipitated was, on account of the small quantity of ethylamine present, too small to be properly recrystallized.

No. 2 was the chloroplatinate of diethylamine; a platinum-salt made from that chloride, insoluble in absolute alcohol, gave 44·3 per cent. platinum, which agrees well with the amount in the chloroplatinate of ammonium. No phenylic alcohol or its compounds were found; and according to the experiments of Long (not yet published) on the oxidation of phenylic alcohol, he always obtained, except where he used spongy platinum, a resinous mass.

From the above experiments, it appears that by the action of nitrous acid, nitric acid, binoxide of manganese and sulphuric acid, permanganate of potash*, potash†, and in some cases by the presence of acids alone‡ (sulphuric and hydrochloric), on the organic bases in the presence of water, water only is decomposed in the first stage of the reaction; and the fact that radicals in the ammonia are replaced by hydrogen by degrees makes it plausible that we may by these means be able to determine the constitution of the natural organic bases.

I am at present experimenting with narcotine, and hope shortly to be able to determine its constitution.

In conclusion, I may here thank Dr. Holzmann for his assistance in carrying out the above experiments.

* By the action on aniline, ammonia has been obtained.
† By its action on the amides.
‡ As in the case of asparagine, benzamide, &c.

THE CHEMICAL GAZETTE.

No. CCCXCIII.—March 1, 1859.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Investigation of the Salts of Chromium. *By* E. Fremy.

It is well known that the violet salts of chromium, such as the sulphate or the sulphate of alumina and chrome, are modified and converted into uncrystallizable bodies of a fine green colour under the influence of a slightly raised temperature, and also that these salts, when treated with an excess of ammonia, furnish liquids of a violet-rose colour. As these facts relate to the curious question of isomerism, they have been made the subject of important investigations by Berzelius, Schrötter, and Löwel.

Nevertheless they have still remained obscure, and we neither know the difference which exists between the violet salts and those which have been rendered green by the action of heat, nor the composition of the rose-coloured compounds formed by some salts of chromium under the influence of ammonia.

The author's object has been to throw some light upon this interesting subject, which presents certain analogy to those of which he has treated in his previous researches upon the hydrates and amide bases formed by cobalt. He divides his memoir into three parts:—

The first treats of the modifications produced in hydrated sesquioxide of chromium and its salts by heat.

The second makes known a new class of bodies, to which the author gives the name of *amido-metallic compounds*.

In the third are described the substances resulting from the decomposition of the preceding amide bodies, and the investigation of a new base, containing the elements of ammonia and sesquioxide of chromium.

1. *Modifications produced by heat in Sesquioxide of Chromium and the violet Salts of Chromium.*

When a violet salt of chromium is precipitated by ammonia it furnishes a hydrate, which, when dried *in vacuo*, is represented by the formula

$$Cr^2O^3, 9HO.$$

This hydrate is distinguished from another, to be referred to hereafter, by its solubility in acetic acid, ammonia, and dilute solution of potash.

Various, and apparently feeble, influences modify this hydrate,—thus the action of boiling water and of concentrated saline solutions, desiccation in the open air or *in vacuo* continued for several days, or friction for a few moments, are sufficient to cause this hydrated sesquioxide of chromium to lose its solubility in the above reagents.

This modification of the oxide is due to an isomeric change, and not to dehydratation; it can hardly be supposed, for example, that an oxide of chromium which loses its solubility in acetic acid and potash, by being kept for a few days in cold water, can undergo this modification in consequence of a dehydratation taking place in the midst of the water, and analysis shows no difference between these hydrates.

As the existence of the two isomeric states of oxide of chromium serves as the foundation of the author's investigation, and readily elucidates various phænomena which have hitherto been unexplained, the author has given different denominations to the two hydrates. He retains the name of *sesquioxide of chromium* for the well-known oxide, which, having undergone the action of boiling water, or the prolonged influence of cold water, is insoluble in acetic acid, in potash, and in ammonia; and gives that of *metachromic sesquioxide* to that which is still soluble in the above reagents, and which is obtained by precipitating a violet salt of chromium by ammonia in the cold. When the latter has become converted into ordinary oxide, it may be made to resume its former state by boiling it with an excess of acid and precipitating it with ammonia: this fact was observed by Löwel.

After ascertaining the existence of two isomeric states of oxide of chromium, the author was in a position to investigate the changes which the salts undergo by the action of heat, and to see whether this conversion of a violet into a green salt is due to a dehydratation of the molecule of the salt, to the production of a new acid or basic salt, or to an isomeric modification of the base contained in the salt. Upon this point his experiments leave no doubt; after ascertaining by numerous trials that when a violet salt of chromium becomes green by ebullition, there is no elimination either of acid or base, he precipitated the oxide of the green salt by ammonia, and compared it with that obtained from the violet salt, when he found that there were strongly marked differences between the two bases, and that the oxide of the green salts had become insoluble in dilute potash and in ammonia,—in fact the ebullition had converted the metachromic oxide into ordinary oxide of chromium. The changes above referred to are therefore due to an isomeric modification of the oxide in the salt.

2. *Amidochromic Compounds.*

The two isomeric states of oxide of chromium do not behave in the same way in the presence of ammonia. The oxide modified by

heat does not react upon ammonia; whilst the metachromic oxide, in contact with ammonia, changes its colour, acquires a violet tint, and gives origin to an amide-compound which appears to be produced by the combination of equal equivalents of oxide of chromium and ammonia; this body, when heated, evolves water and much ammonia, and leaves a residue of anhydrous oxide of chromium.

Ammoniacal salts have no action upon metachromic oxide, but when it is submitted to the double influence of ammonia and an ammoniacal salt, it presents a perfectly new phænomenon. It then dissolves completely, and produces compounds which are remarkable for their fine violet-rose colour. The author has isolated these bodies by precipitating the liquids with alcohol, and preserving the amido-metallic substances from the decomposing action of the alcohol by rapid drying *in vacuo*.

All ammoniacal salts are capable of effecting the solution of metachromic oxide, under the influence of ammonia, and of giving origin to coloured compounds, the general properties of which are indicated by the description here given of that produced by muriate of ammonia.

This body, when dry, is of a fine violet colour; when dissolved in water, it gives the liquid an intense violet-rose colour; the chemical characters of the elements of which it is composed are entirely masked; its reaction is scarcely alkaline, although its molecule contains a considerable proportion of ammonia; nitrate of silver produces no precipitate in its solution, and yet it contains the elements of muriatic acid; the ordinary reagents do not reveal the presence of chromium, although oxide of chromium is the base of the compound.

But when the solution is boiled, the elements just mentioned become sensible; considerable quantities of ammonia are evolved; the hydrated sesquioxide of chromium is precipitated; and nitrate of silver then indicates a considerable proportion of muriate of ammonia in the liquid.

The bodies composing this singular substance separate in a proportion expressed by the formula

$$2(ClH, NH^3), 4NH^3 + 3Cr^2O^3 + Aq.$$

This decomposing action of water recalls the conversion of the amides into ammoniacal salts, and this has induced the author to give the name of *amido-metallic bodies* to the substances just mentioned.

These phænomena proving that ammonia reacting upon a metallic oxide and upon any salt of ammonia, may form compounds in which the elements have lost their distinctive characters, just as cyanic acid loses its generic properties when it forms urea in presence of ammonia in the beautiful experiments of M. Wöhler, render it impossible not to see that in this case mineral chemistry is completely confounded with organic chemistry.

3. *Products of the Decomposition of the Amidochromic Bodies.*

When the solution of an amidochromic body is exposed to the air for some time, it is soon decomposed by reacting upon the elements of water; the ammonia is evolved, the ammoniacal salt is regenerated, and an insoluble violet body is deposited; the latter is not crystallized, but forms small rounded transparent grains, with an opaline lustre.

This substance, like that which produced it, is an amide; its composition is simple, for it only contains the elements of oxide of chromium and ammonia; the action of boiling water is sufficient for its complete decomposition, when the elements separate in the following proportions:—

$$Cr^2O^3, NH^3, 12HO.$$

Acids do not simply convert this body into a salt of chrome and an ammoniacal salt, but they give origin to a new ammoniaco-metallic base, which the author calls *roseochrome*, and in which 1 equiv. of oxide of chromium combines its molecule with 4 equivs. of ammonia; this double base should consequently be represented by the formula

$$Cr^2O^3, 4NH^3.$$

The decomposition of the insoluble violet amidochromic body under the influence of acids may be explained in the following manner:—

$$4(Cr^2O^3, NH^3) + 12SO^3 = 3(Cr^2O^3, 3SO^3) + \underbrace{(Cr^2O^3, 4NH^3), 3SO^3}_{\text{Sulphate of roseochrome.}}.$$

The insoluble violet amido-chromic body is not the only compound capable of giving origin to the new roseochromic base; this is very easily produced by the action of cold concentrated acids upon the soluble amidochromic compounds obtained by precipitation by alcohol from the rose-coloured liquids resulting from the action of metachromic oxide upon a mixture of ammonia and an ammoniacal salt.

The roseochromic salts are represented by the following general formula:—

$$(Cr^2O^3, 4NH^3), 3A.$$

Their solutions are of a nearly pure rose-colour; the muriate crystallizes with the greatest facility, and its analysis led to the formula

$$(Cr^2O^3, 4NH^3)\,3HCl.$$

This salt crystallizes from an acid liquid in fine regular octahedra; it forms crystallized double chlorides with platinum and mercury.

The base roseochrome does not appear to be the only substance which may be formed by the reaction of ammonia upon oxide of chromium. Pure water decomposes muriate of roseochrome, producing a new salt which crystallizes in fine, right rhomboidal prisms and another saline compound, far more soluble than the preceding. These salts appear to contain different bases. The author therefore

thinks that the series of amidochromic bases will be numerous, and that it will correspond with the series of cobalt-bases described by him in a previous memoir. Sesquioxide of cobalt form the following amide-bases:—

$$Co^2O^3, 4NH^3,$$
$$Co^2O^3, 5NH^3,$$
$$Co^2O^3, 6NH^3.$$

Roseo-chrome, $Cr^2O^3, 4NH^3$, would therefore be the first term of a series of double bases, resembling those produced by cobalt.

The author remarks that the facts observed with regard to the amido-metallic compounds are not sufficiently numerous to enable them to be generalized with safety. However, he calls attention to a remarkable consideration relating to the capacity of saturation of the amido-metallic bases.

The base roseochrome, $Cr^2O^3, 4NH^3$, combines, like sesquioxide of chromium, with 3 equivs. of acid to form neutral salts; the 4 equivs. of ammonia which enter into its molecule have therefore no influence upon the capacity of saturation of the double base, which behaves, in presence of acids, like a sesquioxide resulting from the combination of 2 equivs. of a radical with 3 equivs. of oxygen. This is also the case with the amido-cobaltic bases, containing as much as 6 equivs. of ammonia; these only saturate 3 equivs. of acid, like the sesquioxide of cobalt which forms the base of their molecule. Organic chemistry presents numerous examples of bodies which thus lose their capacity of saturation by forming complex molecules.

From these facts the author draws the following general conclusions:—

1. It has been proved in this memoir that a metallic oxide may affect two isomeric states, and form two series of salts presenting marked differences in their general properties, due to the conditions of the oxide entering into the saline combination. If this observation extends to many metallic oxides (as seems to be probable), it will be easy henceforward to explain the modifications which certain salts undergo in their colour and chemical properties, under the influence of heat. The isomeric modification of the oxide would be the cause of the changes in the properties of the salt.

2. It is well known that several oxides, such as those of platinum, mercury, iridium, cobalt, &c., are capable of associating their molecule with ammonia, forming double bases which present some analogy to the organic alkalies; but this is the first time that a metallic oxide, such as metachromic oxide, has been found to act simultaneously upon ammonia and ammoniacal salts to form compounds in which the three elementary bodies have lost their essential properties.

3. In his researches upon cobalt the author produced amido-metallic bases by the direct action of ammonia upon salts of cobalt; in the present case he has generated the amidochromic bases by placing metallic amides in presence of acids.—*Comptes Rendus*, Dec. 6, 1858, p. 883.

New Observations on Sulphur. *By* M. Berthelot.

In the investigation of the modifications of sulphur and the relations existing between them and the nature of the sulphuretted compounds, it is essential that care should be taken not to destroy these conditions by the very processes destined to prove their existence. This difficulty is inherent in the nature of such researches. Thus, in all these phænomena, we are compelled to seize the fugitive indications of delicate differences correspondent with the nascent state. These differences may be effaced by various perturbing causes, some physical, others chemical. I have carefully studied these perturbing causes, and defined them as far as possible. In all cases, it is evident that the inductions deduced from observations are legitimate in proportion as there has been less disturbance in the phænomena.

Such are the conditions which I have always endeavoured to realize. The investigations to which my theories have given rise also agree in most points with my experiments and observations; and if there are some partial differences, I think they are due precisely to the causes just indicated,—I mean the employment of conditions very different from those in which I have endeavoured to place myself.

1. The facts observed by M. Cloëz with regard to the decomposition of the chlorides of sulphur and the hyposulphites, agree with my observations, and with the interpretation which I have given of them; for that chemist regards the soft, insoluble state as the normal condition of sulphur at the moment when it is disengaged from its compounds, a condition which has but little stability, and which is modified especially under the influence of a slow decomposition: this is exactly the view developed by me.

2. The electrolysis of sulphurous acid has also furnished M. Cloëz with the results announced by me.

But he indicates opposite results with regard to sulphuretted hydrogen, and this requires explanation.

To investigate the electro-chemical decomposition of a body, it is not sufficient to immerse the two poles of a battery in its solution, and to attribute all the effects produced to the direct action of the current. Thus, to cite a very general example, the electrolysis of sulphate of copper and of metallic salts, furnishes the metal at the negative pole, but this metal is produced, according to circumstances, sometimes by the direct action of the current, and sometimes by a secondary action caused by the hydrogen of the water. All physicists are acquainted with these phænomena; they know that the secondary actions are produced more easily, as the electrolysis is more rapid, or, if I may employ the word, more brutal.

I think that this is the case in the electrolysis of sulphuretted hydrogen; the sulphur deposited at the positive pole may result either from a direct action of the current, or from various secondary actions. In my first memoir (Annales de Chimie et de Physique, 3^{e} série, xlix. p. 449) I had already considered these secondary actions, and foreseen that they might furnish "amorphous and insoluble sulphur." But by operating slowly and regularly, to avoid them as much as possible, I have obtained upon the positive

pole a deposit of octahedric sulphur, which was whitish and pulverulent from the first moment of the experiment, similar to that formed in the spontaneous decomposition of solutions of sulphuretted hydrogen. The facts announced by M. Cloëz show that it is possible to arrive at a different result, no doubt by operating more rapidly. But the insoluble sulphur which he has obtained appears to me to result not from a direct electrolysis, but from a secondary oxidation. Perhaps, in an experiment carried on too rapidly, the sulphuretted hydrogen which surrounds the positive pole may be completely destroyed before it is replaced by that contained in the rest of the liquid, and sulphurous acid may be formed by the reaction of the nascent oxygen upon the sulphur first deposited; now, this sulphurous acid may act in its turn upon the sulphuretted hydrogen, forming insoluble sulphur. Without going further, this is sufficient to show that the conditions of phænomena may be entirely changed, if experiments are hurried. However, they require a more profound experimental investigation, which, although very delicate, I believe to be possible, starting from the opinions of physicists with regard to electrolysis.

3. The greater aptitude for oxidation presented by insoluble sulphur as indicated in my memoir, has been demonstrated more completely by M. Péan de Saint-Gilles. It does not depend on the dissimilar state of division of the insoluble and octahedric sulphur, for it has been established by comparison, by operating on the one hand upon insoluble sulphur, and on the other upon the same sulphur changed by contact action in the cold into crystallizable sulphur, its state of division remaining exactly the same.

This point is therefore in accordance with my opinions and experiments.

With regard to the difference between my observations and those of M. Cloëz upon the formation of sulphuret of iron, this is not due to an error of analysis on my part, for I have ascertained that no sulphate, or free hydrogen, or sulphuretted hydrogen was formed in sensible proportions in my operations; protosulphuret of iron was their sole essential product, which justifies my analytical process. As to the employment of a solution of potash to separate the free sulphur from its mixture with various sulphuretted and sulphurable compounds, this method, proposed by M. Cloëz, will no doubt appear dangerous to most chemists.

I have operated upon small quantities, avoiding all evolution of heat, and in such a way as to render the reaction slow and regular; whilst M. Cloëz, operating upon greater masses, appears to me to have placed himself in conditions of sudden reaction, accompanied by a lively evolution of heat. The difference must be attributed to this cause, to certain anomalies which that chemist, like myself, appears to have observed, and which I cannot yet explain, and lastly, perhaps, to the employment by him of insoluble sulphur recently prepared, and still retaining that softness and plasticity which I have indicated, and which partially change the nature of its reactions, until in course of time it has acquired its definitive cohesion.

As regards the combination of sulphur and mercury, as it is not capable of measurement and I have stated nothing about it, I shall pass it in silence.

I will only add a word in relation to the changes of state which sulphur undergoes when in contact with certain agents before combining with them. I have discovered these phænomena and defined their precise conditions—the complete change of insoluble sulphur into octahedric sulphur in contact with potash and the alkaline sulphurets, the partial change of octahedric into insoluble sulphur at the moment of its fusion in contact with nitric acid, &c. I have explained the inductions deduced from these observations, but it would be to attribute an erroneous opinion to me gratuitously to make me say that the same thing necessarily occurs in the formation of all combinations.—*Comptes Rendus*, Dec. 6, 1858, p. 910.

On the Yellow Colouring Matter and the Tannic Acid in Thuja occidentalis. *By* M. KAWALIER.

[Concluded from page 66.]

Tannic acid of the green parts of Thuja occidentalis.—Kawalier has also examined the tannic acid which is contained in *Thuja* together with thujine and thujigenine. When the precipitate which is produced by solution of acetate of lead in the aqueous residue of the alcoholic decoction, freed from wax and resin, is decomposed by sulphuretted hydrogen, and the fluid is heated and filtered whilst hot, thujine is obtained in solution from the tannic acid. After the thujine has crystallized, the mother-liquor is evaporated to dryness, and the residue extracted with a mixture of anhydrous alcohol and æther. After filtration, this solution is rapidly evaporated in the water-bath, and the residuary acid is triturated and placed over sulphuric acid *in vacuo*. It forms a pale brownish powder, the aqueous solution of which has an astringent taste. When heated upon platinum-foil it burns, and leaves a voluminous coal, which is slowly combustible and leaves no ash. Solution of perchloride of iron at first produces a very dark reddish-brown colour, and a precipitate is formed by long standing. Lead-salts produce beautiful yellow precipitates. The acid exhibits in general all the reactions of pinitannic acid, which was discovered by Kawalier in the leaves of *Pinus sylvestris*. Analysis:—

C	53·56	14=84	53·84
H	5·45	8 8	5·12
O	40·99	8 64	41·04

The precipitate which is produced by basic acetate of lead in the fluid filtered from the precipitate caused by the neutral acetate, and which contains thujine and pinitannic acid, also contains a portion of pinitannic acid together with some thujigenine. The mother-liquor of thujigenine, evaporated *in vacuo*, leaves this acid as a

residue. Analysis:—

C	53·78
H	5·55
O	40·67

These portions of pinitannic acid obtained in the preparation of thujine and thujigenine, were also employed by Kawalier for decomposition by acids. It was stated in the investigation of Kawalier upon *Pinus sylvestris*, that a red product of decomposition is produced from pinitannic acid by the action of sulphuric and muriatic acids. The solution of pinitannic acid was treated with sulphuric acid and with muriatic acid, and in both cases the same red product was obtained by heating it on the water-bath. The red product, washed with water on a filter and then boiled with water, dissolves partially therein. A portion remains undissolved, and the dissolved portion separates with a tile-red colour, on the cooling of the aqueous filtrate. The dissolved portion, and also that which remained undissolved, were dried *in vacuo* over sulphuric acid. The soluble portion is given under I., the insoluble under II.

I. The reddish-brown, insoluble, or rather difficultly soluble part gave the following numbers on analysis:—

	I.	II.	III.
C	58·49	58·40	58·22
H	4·67	4·77	4·65
O	36·84	36·83	37·13

III. is the analysis of the red body which was prepared by Kawalier from the leaves of *Pinus sylvestris*.

The acid fluid which was separated from the red product of decomposition, reduced an alkaline solution of sulphate of copper like grape-sugar, after the acid and the small quantity of the red body which was dissolved in it had been removed. This fluid was evaporated in the water-bath, when it left an amorphous residue of a brownish-yellow colour, which had no sweet taste, and exhibited the following composition:—

C	47·02	12	= 72	47·06
H	5·84	9	9	5·88
O	47·14	9	72	47·06

The composition of this body, which possesses no property of sugar except the faculty of reducing oxide of copper, suits equally well with the formula $C^{28}H^{21}O^{21}$, as with $C^{12}H^{9}O^{9}$, both requiring the same centesimal composition; thus—

			Calculated.
C	28	= 168	47·06
H	21	21	5·88
O	21	168	47·06

It is at any rate certain that, from the concordance of the analyses of the pinitannic acid from *Thuja occidentalis* and *Pinus sylvestris*, the centesimal composition of this acid is established, and also that

of the red product of decomposition which is formed from pinitannic acid by the action of acids. For pinitannic acid Kawalier had set up the formula $C^{14} H^{8} O^{8}$; it might easily be proved by tripling the formula, which will then be $C^{42} H^{24} O^{24}$, that this substance is homologous with thujine $= C^{40} H^{22} O^{24}$, and consequently must undergo a decomposition into sugar, and a body homologous with thujetine. But there is no proof of the production of sugar, and the analyses of the red product of decomposition do not agree with a formula which should contain 30 equivs. of carbon. In the same way the formula $C^{14} H^{8} O^{8}$ might be quadrupled to $C^{56} H^{32} O^{32}$, and the red body be expressed by $C^{44} H^{21} O^{21}$. It appears to Dr. Rochleder, however, that all such assumptions deserve no further examination.

The so-called oxypinitannic acid was also treated with sulphuric acid, in order to prepare sugar from it; but when the red product of decomposition was removed, there remained an amorphous substance, which contained 42·60 per cent. C and 6·80 per cent. H, and had no more resemblance to sugar than the body above mentioned.

The leaves of *Pinus sylvestris* contain pinitannic acid in the spring. Oxypinitannic acid, however, is not present, and instead of the acid $C^{28} H^{13} O^{15}$, the acid $C^{28} H^{15} O^{13}$ was once obtained from the leaves: it had been precipitated from the aqueous solution by sulphuric acid. Analysis of the acid dried at 212° F.:—

C	58·45	28	168	58·54
H	5·28	15	15	5·22
O	36·27	13	104	36·24

This acid, which might be called tannopinic acid, is easily oxidized, as is also the red product of decomposition which it furnishes by the action of muriatic or sulphuric acid with the assistance of heat. It would very easily happen that a small deficiency of hydrogen would be found on analysis, if this body had the opportunity of coming in contact with the oxygen of the atmosphere whilst in a hot solution. The leaves which contained tannopinic acid were collected at Easter four years ago, and investigated by Kawalier; the leaves which contained oxypinitannic acid were, on the contrary, obtained about Christmas 1852. Consequently either tannopinic acid undergoes an oxidation in the course of the first months of winter, and thus becomes converted into oxypinitannic acid,—

$$\underset{\text{Tannopinic acid.}}{C^{28} H^{15} O^{13}} - H^{2} + O^{2} = \underset{\text{Oxypinitannic acid.}}{C^{28} H^{13} O^{15}}$$

or the oxypinitannic acid undergoes a reduction at the commencement of spring, and becomes converted into tannopinic acid, for $C^{28} H^{13} O^{15} + 2H - 2O = C^{28} H^{15} O^{13}$. It is certain, however, that pinitannic acid is present at both periods.

Kawalier formerly discovered two acids in the bark of old trees, collected about Christmas, and called them pinitannic acid and cortepinitannic acid. Four years ago, at Easter, he collected and

examined the bark of some young trees. The trees might be 20—25 years old. The bark was cut up into small pieces, extracted with alcohol of spec. grav. 0·951, the alcohol distilled off in the water-bath, the residue mixed with water, and again distilled to remove the last traces of alcohol. The aqueous residue of distillation is brownish red; a sticky resin was deposited from it. The resin was removed by a filter, and the filtrate mixed with solution of sugar of lead, as long as a precipitate was produced thereby. The precipitate was washed with water, and treated with dilute acetic acid in insufficient quantity to dissolve it. The acetic solution was filtered, the undissolved portion again treated with an insufficient quantity of dilute acetic acid, and the dissolved part separated by filtration. The third portion obtained by acetic acid was also separated by filtration of the undissolved portion of the precipitate. The portion of the precipitate finally left undissolved contains a portion of resin. The fluid which had been filtered from the precipitate produced by acetate of lead, furnishes a yellow precipitate with basic acetate of lead. The two solutions first obtained by the treatment of the precipitate produced by acetate of lead, with dilute acetic acid, were mixed together, as being of the same nature, but the third solution was set aside by itself. The acetic solutions were mixed with basic acetate of lead, and the precipitate produced was collected on a filter, and washed with water. The third solution was treated in the same way by itself.

The two precipitates were decomposed under water by sulphuretted hydrogen, the fluids separated from the sulphuret of lead by filtration, the sulphuretted hydrogen expelled by a current of carbonic acid whilst the fluid was heated, and the two solutions were reduced to half their volume in a current of carbonic acid.

In 24 hours the acid is deposited on the walls of the vessel in the form of crusts of a pale brownish colour, with a tendency to red. It was dried at 212° F. When pounded, it forms a reddish-brown powder of an astringent taste, the aqueous solution of which is rendered dark green by perchloride of iron. This colour passes to reddish brown by standing. In time a blackish-green precipitate is deposited. When heated with muriatic or sulphuric acid, a fine red precipitate is formed in the aqueous solution: the red substance which is deposited may be separated by filtration. It has nearly the same composition as the acid from which it is produced. After the acid which was employed for its conversion has been removed by suitable means, and a small residue of the red product has been got rid of by basic acetate of lead, the lead by sulphuretted hydrogen, and the sulphuretted hydrogen by heat, the result is a clear, colourless fluid, which behaves towards Fehling's fluid like a solution of sugar.

7·2615 grms. of acid gave, according to Fehling's method, 0·3948 grm. of sugar ($=C^{12}H^{12}O^{12}$). On evaporation the solution left a colourless, sweetish residue, which, when heated upon platinum-foil, became carbonized and burnt like sugar.

The analysis of this acid, which is distinct from pinicortanic and cortepinitannic acids, and which may be called tannecortepinic acid,

gave the following composition:—

C	60·32	60·59	60·34	28	=168	60·65
H	4·73	4·74	4·81	13	13	4·69
O	34·95	34·67	34·85	12	96	34·66

The similarity of its composition with that of the acids in the leaves of *Pinus sylvestris* will be seen at once.

If the sugar produced in the decomposition be regarded as essential and the formula of the acid be established in accordance with this view, this formula would contain $C^{322}H^{152}O^{144}$, and consequently would be broken up into $C^{12}H^{12}O^{12}$ and $C^{320}H^{142}O^{134}$. Further reference to such a view is superfluous. Upon the production of small quantities of sugar in the treatment of bodies of this kind with acids, the author expresses himself more in detail in the course of this memoir.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xxix. p. 10.

On the Products of the Oxidation of the Acetones. *By* C. Friedel.

Starting from the hypothesis that the acetones are aldehydes in which 1 equiv. of hydrogen is replaced by an alcoholic radical, it must be supposed that, when placed in circumstances in which the aldehydes give origin to acids, the acetones would furnish the corresponding æthers.

Aldehyde. $C^4H^3O^2+O^2$ (H) — Acetic acid. $C^4H^3O^2$ (H) $\}O^2$.

Acetone $C^4H^3O^2+O^2$ (C^4H^3) — Acetate of methyle. $C^4H^3O^2$ (C^4H^3) $\}O^2$.

This most conclusive experimental confirmation of Gerhardt's theory upon these bodies is furnished by the author; by oxidation the acetones are converted into æthers.

When a tube filled with acetone is suspended in a large balloon, at the bottom of which is some platinum-black, the acetone may be poured over the platinum-black in the course of a day or two without any danger of too brisk an action. By renewing the air in the balloon from time to time, an agreeable ætherial odour different from that of acetone, is soon perceived. In eight days a little water was added in order to collect the products more completely; these were transferred into a small balloon, distilled on the water-bath, dried over chloride of calcium and redistilled. The liquid obtained boiled at about 140° F., and was not soluble in water in all proportions like acetone. On analysis it gave numbers closely approaching those of acetate of methyle, but with a slight excess of carbon and hydrogen, probably due to a residue of acetone not removed by washing with water.

	Liquid obtained.		Acetate of methyle.	Acetone.
	I.	II.		
Carbon	49·42	49·62	48·64	62·06
Hydrogen ..	8·73	8·48	8·10	10·34

This liquid was heated in the water-bath, in a sealed tube, with an aqueous solution of potash. When the tube was opened and the contents distilled, a liquid boiling at 149°—158° F. was obtained. It was methylic alcohol mixed with acetone; when distilled with oxalic and sulphuric acids, it furnished crystals of oxalate of methyle.

The potash was partly combined with acetic acid, from which it was separated by distillation with sulphuric acid. The distilled acid liquid, saturated with ammonia and precipitated by nitrate of silver, furnished a salt containing 64·49 per cent. of silver. Acetate of silver contains 64·66 per cent.

From these facts it appears that acetone is converted into acetate of methyle in the presence of air and platinum-black.

Butyrone is oxidized much less rapidly, but when exposed to the air for eight days in an open balloon with platinum-black, it acquired a strong odour of butyric æther, and analysis showed that it contained about one-ninth of butyrate of propyle.

A remarkable fact which renders it almost impossible to separate the acetone and the æther which it produces by oxidation, is that these compounds always distil nearly at the same temperature, so that the introduction of 2 molecules of oxygen into an acetone appears scarcely to modify its boiling-point.

Acetone boils at 132°·8 F.; acetate of methyle at 136°·4 F.; butyrone at 293° F.; butyrate of propyle, judging from the boiling-point of butyrate of æthyle, should boil at about 280° F. Methylobenzoyle boils at 388°·4 F.; methylobenzoic æther at 389°·3 F. This difficulty rendered it important to find an agent of oxidation which would act more rapidly and more completely than platinum-black.

Ordinary acetone is converted almost instantaneously into methyl-acetic æther by permanganate of potash. By distilling acetone twice with an excess of permanganate of potash, the author obtained a liquid having an agreeable ætherial odour, and boiling between 136°·4 and 145°·4 F. Its analysis gave,—

		Acetate of methyle.
Carbon	48·15	48·64
Hydrogen ..	8·44	8·10

The liquid remaining in the balloon effervesces with acids; when distilled with tartaric acid, saturated with caustic soda, and mixed with nitrate of silver, it gave, on boiling, the characteristic reduction of formic acid, and when filtered and evaporated, a crystallization of acetate of silver. A portion of the acetone is entirely oxidized, giving origin to carbonic acid and water. The formic and acetic acids are probably produced by the action of the potash of the permanganate upon a portion of the acetate of methyle formed. The products are acetate of potash and methylic alcohol, which is immediately oxidized and converted into formic acid.

Dry permanganate of potash oxidizes acetone far more slowly; this may have led M. Péan de Saint-Gilles into error, as he stated some time since that permanganate of potash has no action upon this liquid. However, after four or five distillations, even when

acetone rectified several times over cholride of calcium is employed, the distillate contains a considerable quantity of acetate of methyle.

Solution of permanganate of potash also acts upon butyrone and upon methylobenzoyle when boiled, but the oxidation appears to go too far. With butyrone, the distillate contains a portion of the pure primitive body:—

	Butyrone.	Found.
Carbon....	73·68	73·15
Hydrogen..	12·28	12·21

The liquid remaining in the balloon contains butyrate of potash. These acetones therefore require other means of oxidation, and we must probably recur to platinum-black.

It would be the more interesting to find a process applicable to all the acetones, as besides the facility which it would furnish for preparing some æthers which it is difficult to obtain otherwise, the conversion of the acetones into æthers affords a means of studying the constitution of certain isomeric acetones,—to ascertain, for example, whether in the distillation of a mixture of butyrate and propionate of lime, æthylobutyryle or propyleacetyle is obtained.—*Comptes Rendus*, Dec. 6, 1858, p. 921.

Note on the Preparation of the Double Cyanides of Platinum. *By* Dr. W. Knop.

Some years ago the author described a number of double cyanides of platinum, which may be arranged in three series.

The first series contains compounds having the constitution of Gmelin's salt, KCy, PtCy.

A second series is indicated by the beautiful metallic, cupreous sesquicyanide of potassium and platinum, $2KCy + Pt^2 Cy^3$, which was obtained by passing chlorine into a solution of Gmelin's salt, and by the corresponding ammonium salt.

The third series was indicated by the discovery of the compound of bicyanide of platinum with chloride of potassium, $KCl, PtCy^2$; the author obtained it by treating the two preceding salts with nitro-muriatic acid at a boiling heat.

For the preparation of all these salts we start from Gmelin's salt. Gmelin prepared the protocyanide of platinum and potassium by fusing ferrocyanide of potassium with spongy platinum; Meillet prepared it by boiling a solution of perchloride of platinum with cyanide of potassium.

As the author employed large quantities of Gmelin's salt in his investigations, it became a matter of importance to him to find out a more productive method, and he succeeded in preparing this salt by means of protochloride of platinum.

The preparation of Gmelin's salt from protochloride of platinum and cyanide of potassium requires nothing more than some familiarity with the preparation of the protochloride of platinum; by practice the degree of heat must be accurately learnt, at which perchloride of platinum is exactly reduced to protochloride. If it be overheated, a corresponding amount of the protochloride becomes

converted into metal, and the preparation must be commenced again. The decomposition of the protochloride of platinum and cyanide of potassium then takes place without anything further; a solution of chloride of potassium and Gmelin's salt is obtained, and the salts are separated by crystallization.

In operating with large quantities, this mode of preparation is easy, and always leads with certainty to the desired result. It is not so well adapted to the preparation of small quantities of the salt. This may be effected as follows:—

Monosulphuret of platinum is prepared by boiling the ordinary solution of perchloride of platinum with a slight excess of hyposulphite of soda. The solution is boiled until it becomes deep brown-red, then greatly diluted with water, and treated with an excess of muriatic acid. The vessel is then placed upon the sand-bath, and left for several hours or a whole day; the temperature may approach the boiling-point of the fluid. As soon as all the sulphurous acid is dispelled, the platinum lies at the bottom in the form of brown sulphuret of platinum, mixed with the sulphur deposited by the decomposition of the excess of hyposulphite of soda; the supernatant fluid is limpid. This sulphuret of platinum may be very easily washed.

The washed precipitate is rinsed off the filter, and treated with solution of potash; cyanide of potassium is then added, and the whole is heated for some time. A clear yellow or brownish solution is obtained, and when this is sufficiently concentrated, Gmelin's salt crystallizes from it.

The author has not tried whether the corresponding ammoniacal salt may be obtained in the same way.

Since he prepared the salts above referred to, several others of the same kind have been discovered by other chemists; they all form members of the three series indicated. Amongst the products which the author obtained from the ammoniacal salt corresponding with Gmelin's salt, by treating it with nitromuriatic acid, he observed some beautifully crystallized salts; these he could not investigate further, from the large amount of platinum required for this purpose, but he supposes that they may perhaps belong to other series.—*Chemisches Centralblatt*, 1859, ii. p. 17.

Note on Acetate of Alumina. *By* C. Tissier.

If gelatinous alumina be dissolved in acetic acid so as to obtain a liquid marking 8° or 9° of Beaumé, and this solution be kept in well-stoppered bottles, a white precipitate is observed after the lapse of a certain time (from a week to several months) at the bottom of the bottles. This precipitate, which is more or less crystalline, contains the whole of the alumina, whilst the liquid has become strongly acid, and only contains traces of that base. The precipitate is insoluble in water, but dissolves with difficulty in dilute acids, and with great facility in caustic alkalies.

According to Gay-Lussac, solutions of acetate of alumina containing a little sulphate of potash or soda are rendered turbid by heat, but regain their transparency on cooling. The author examined

the precipitate above mentioned for potash and soda, but only found insignificant traces of those two bodies, and on analysing several of the crystalline deposits formed in different liquids and in very different periods of time, he found that they all possessed a constant composition, corresponding with the formula

$$Al^2O^3, 2(C^4H^3O^3)+6HO,$$

that is to say, instead of 3 equivs. of acetic acid, necessary to form the neutral salt, they only contain 2 equivs. The rest of the acetic acid remains in solution.

The process of analysis adopted by him consisted in dissolving a certain weight of the acetate to be analysed, in a known weight of an alkaline liquid. The difference in the strength of the liquid before and after the solution furnishes the amount of acetic acid combined with the alumina. Three analyses made with different precipitates gave—

	I.	II.	III.	Average.	Calculated.	
Alumina	33·98	34·31	34·80	34·36	33·55	Al=13·75
Acetic acid	66·02	65·69	65·20	65·64	66·45	

Formula $Al^2O^3, 2(C^4H^3O^3)$.

The water was determined by the calcination and incineration of the salt dried at 77° F., and deducting the actual weight of that base and the calculated weight of the acid. The average of two determinations gave—

		Calculated $Al^2O^3, 2(C^4H^3O^3)+6HO$.
Alumina....	24·63	24·83
Acetic acid..	48·77	49·15
Water.....	26·60	26·02

This slow and spontaneous decomposition of acetate of alumina by keeping, without exposure to the least elevation of temperature, may perhaps account for the different results obtained in the application of this compound as a mordant upon printed stuffs, according as it has been kept for a longer or shorter time.—*Comptes Rendus*, Dec. 6, 1858, p. 931.

PROCEEDINGS OF SOCIETIES.

Royal Society.

November 25, 1858. (W. R. Grove, Esq., V.P., in the Chair.)

"Researches on the Phosphorus-Bases."—Phosphoretted Ureas. By A. W. Hofmann, Ph.D., F.R.S.

The existence in the nitrogen-series of a well-defined group of diamines of the formula

$$\left.\begin{matrix} A_2 \\ B_2 \\ C_2 \end{matrix}\right\} N_2,$$

rendered it probable that the continued study of the phosphorus-,

arsenic-, and antimony-bases would lead to the discovery of the corresponding terms,

$$\left.\begin{matrix}A_2\\B_2\\C_2\end{matrix}\right\}P_2,\quad \left.\begin{matrix}A_2\\B_2\\C_2\end{matrix}\right\}As_2 \text{ and } \left.\begin{matrix}A_2\\B_2\\C_2\end{matrix}\right\}Sb_2,$$

which might be designated as diphosphines, diarsines, and distibines; and the further prosecution of this line of thought very naturally suggested the idea of searching for a group of intermediate compounds containing simultaneously nitrogen and phosphorus, nitrogen and arsenic, phosphorus and arsenic, &c., compounds expressed by the formulæ

$$\left.\begin{matrix}A_2\\B_2\\C_2\end{matrix}\right\}NP;\quad \left.\begin{matrix}A_2\\B_2\\C_2\end{matrix}\right\}NAs;\quad \left.\begin{matrix}A_2\\B_2\\C_2\end{matrix}\right\}PAs, \&c.,$$

which might be termed phosphamines, arsamines, phospharsines, &c.

Among the several processes likely to furnish this result, none appeared more promising than the reaction between a monamine and a monophosphine of opposite chemical characters.

In the conception of this idea, I have studied the deportment of cyanic acid and some of its derivatives with phosphoretted hydrogen and its homologues, in the hope of producing combinations similar in constitution to the ureas, but differing from these substances by containing phosphorus in the place of one equivalent of nitrogen.

The action of cyanate and sulphocyanide of phenyle, an account of which I have lately* submitted to the Royal Society, upon triethylphosphine, seemed to include the conditions for the realization of such compounds.

On bringing cyanate of phenyle in contact with triethylphosphine, a most lively reaction ensues; the mixture begins to boil, and the phosphorus-base is apt to be inflamed. On cooling, the liquid solidifies into a crystalline mass, which is insoluble in water, soluble in alcohol and ether, and crystallizes from the latter solvent in beautiful little square tables, tasteless, inodorous, and infusible at 100° C. On submitting this compound to analysis, I was surprised to find that it contained no phosphorus, and that it exhibited the composition of the original cyanate of phenyle, from which it differs so essentially in its properties. This substance is the *cyanurate of phenyle*, generated from the cyanate by simple transposition of the elements. The triethylphosphine participates only indirectly in the reaction; in giving rise to the transformation of the cyanate, the phosphorous body plays the part of a ferment, a comparison which is moreover suggested by the large proportion of cyanate over which the influence of a minute quantity of phosphorus-base extends. A glass rod moistened with triethylphosphine solidifies, almost instantaneously, a considerable quantity of the cyanate. The transformation of the cyanate under the influence of triethylphosphine, into cyanurate, although the principal phase of the reaction, is attended by other changes which I intend to examine more minutely by and by.

Very different results were obtained by substituting for the cyanate the sulphocyanide of phenyle. The reaction between this body and

* Proceedings, vol. ix. p. 274.

triethylphosphine is very violent, and frequently gives rise to the inflammation of the phosphorus-base. The mixture assumes a deep yellow colour, and often deposits splendid yellow needles on cooling; frequently, however, it remains liquid for hours and even for days, but suddenly solidifies, when touched with a glass rod, into a hard, yellow, crystalline mass. This substance is insoluble in water; it dissolves with the greatest facility in alcohol, hot or cold, likewise in warm, less so in cold ether. Recrystallization from boiling ether affords, in fact, the best means of procuring the new body in a state of purity. This end is likewise considerably facilitated, by allowing the sulphocyanide of phenyle to act upon the triethylphosphine in the presence of a considerable quantity of ether.

In the pure state the new compound presents itself in the form of well-defined prisms of uranium-yellow colour, which fuse at 61° C. They cannot be heated much beyond their fusing-point without being altered; at 100° C. they are entirely decomposed, evolving a most peculiar odour, which is also observed on evaporating the ethereal mother-liquor.

The new compound possesses the characters of a well-defined base. Quite insoluble in water, it dissolves in the most dilute acids, forming with some of them, such as hydrochloric and hydrobromic acid, beautifully crystallized saline compounds. From these salts the base may be separated again by cautiously adding either potassa or ammonia. The hydrochloric solution of the base yields with dichloride of platinum a yellow crystalline precipitate, sparingly soluble in water, insoluble in alcohol and ether.

Analysis of the yellow crystals, dried over sulphuric acid, led to the formula

$$C_{26}H_{20}NPS_2,$$

which shows that they are formed by the simple union of the two substances placed in contact:

$$\underbrace{C_{14}H_5NS_2}_{\text{Sulphocyanide of phenyle.}} + \underbrace{C_{12}H_{15}P}_{\text{Triethyl-phosphine.}} = \underbrace{C_{26}H_{20}NPS_2}_{\text{New compound.}}.$$

If we consider urea as a diamine derived from diammonia by the substitution of the diatomic molecule carbonyle $(C_2O_2)''$ for 2 equivs. of hydrogen,

$$\text{Urea } C_2H_4NO_2 = \left.\begin{matrix}(C_2O_2)''\\H_2\\H_2\end{matrix}\right\}N_2,$$

—the simplest perhaps of the many views brought forward regarding the constitution of urea,—the new substance, which formation as well as chemical deportment essentially characterize as an analogue of urea, may be represented by the following formula:—

$$C_{26}H_{20}NPS_2 = \left.\begin{matrix}(C_2S_2)''\\(C_4H_5)_2\\(C_{12}H_5)(C_4H_5)\end{matrix}\right\}NP;$$

that is, urea, the oxygen of which is replaced by sulphur, the hydrogen by ethyle and phenyle, and lastly, half the nitrogen by phosphorus.

The formation of this compound presents considerable interest, not only as an illustration of the remarkable persistence of the type urea, but also as furnishing the first unequivocal instance of the formation of ureas containing no longer any unreplaced hydrogen, the existence of which had as yet remained doubtful.

The new urea forms, as I have stated, a series of well-defined beautifully crystallized salts. Its solution in warm hydrochloric acid solidifies, on cooling, into a crystalline mass, which, when recrystallized from warm water, is obtained in splendid needles of a bright cadmium-yellow colour, often several inches in length. They are decomposed at 100° C., and must therefore be dried over sulphuric acid *in vacuo*. Analysis proved them to contain

$$C_{26}H_{20}NPS_2, HCl.$$

The solution of this salt yields with dichloride of platinum a bright yellow precipitate, which under the microscope is found to consist of small lily-shaped crystals. Dried over sulphuric acid *in vacuo* it contains

$$C_{26}H_{20}NPS_2, HCl, PtCl_2.$$

The hydrochlorate yields also a precipitate with trichloride of gold; the salt is, however, rapidly blackened.

The hydrobromate, both in preparation and properties, resembles the hydrochlorate. Its composition is

$$C_{26}H_{20}NPS_2, HBr.$$

The urea readily combines with iodide of methyle and ethyle. The methyle-compound immediately separates in the crystalline form on mixing an ethereal solution of the urea with iodide of methyle; it is soluble in water, and crystallizes from a boiling solution in beautiful golden-yellow needles, containing

$$C_{26}H_{20}NPS_2, C_2H_3I.$$

The iodide, by the action of chloride of silver, may be converted into the chloride; this yields with dichloride of platinum a fine needle-formed salt, which may be recrystallized without decomposition. The formula of this platinum-salt is

$$C_{26}H_{20}NPS_2, C_2H_3Cl, Pt, Cl_3.$$

When treated with oxide of silver, the iodide furnishes a powerfully alkaline liquid, probably the corresponding base

$$\left.\begin{matrix}[(C_2H_3)((C_2S_2)''(C_4H_5)_3(C_{12}H_5)\underset{H}{N}P)]\end{matrix}\right\}O_2.$$

Scarcely separated, however, this substance decomposes with liberation of sulphocyanide of phenyle, the oxide of methyl-triethylphosphonium remaining in solution. This salt is sufficiently characterized by the readily crystallizable octahedral platinum-salt.

I have not been able to obtain either the sulphate or the nitrate of the urea, probably on account of the great instability of the new substance.

On dissolving the base, even in dilute nitric acid, it is immediately decomposed with separation of sulphocyanide of phenyle, the triethylphosphine being oxidized. The same change is observed when one

of the more stable salts, such as the hydrochlorate, is dissolved in a large quantity of water; the liquid soon becomes turbid from the elimination of oily globules of sulphocyanide of phenyle, and now contains the hydrochlorate of the phosphorus-base.

On adding ammonia to a salt of the urea, similar phenomena are observed. From a concentrated solution, the base is separated without change; but when dilute and hot solutions are employed, the turbidity at first produced disappears, and after a few minutes beautiful crystals of phenyl-sulphocarbamide ($C_{14}H_8N_2S_2$)* make their appearance; at the same time the odour of triethylphosphine becomes perceptible.

With potassa the deportment is perfectly analogous, but the crystals formed after some time are diphenyl-sulphocarbamide (sulphocarbanilide, $C_{26}H_{12}N_2S_2$) instead of phenyl-sulphocarbamide.

On adding to an ethereal solution of the urea a few drops of bisulphide of carbon, the liquid, when gently heated, assumes a deep crimson colour, and deposits, on cooling, the beautiful compound $(C_4H_5)_3P, C_2S_4$, which I have described some time ago†. The mother-liquor yields on evaporation oily drops of sulphocyanide of phenyle.

The deportment of triethylphosphine with sulphocyanide of phenyle induced me to investigate the action of this body upon several other sulphocyanides. The substance which at once suggested itself for examination was sulphocyanide of allyle, mustard-oil. This compound reacts most powerfully with the phosphorus-base. On mixing the two bodies, a powerful evolution of heat takes place, and the mixture assumes a deep brown colour, but does not solidify either on cooling or on agitation. After several days' standing, however, very large well-defined crystals are deposited which unfortunately are contaminated with the brown colouring matter of the solution. I have not yet succeeded in getting them perfectly white, and have therefore not analysed them. Their formation, however, and their general characters leave no doubt that they are the corresponding allyle-compound,

$$C_{20}H_{20}NPS_2 = \left.\begin{matrix}(C_2S_2)'' \\ (C_4H_5)_2 \\ (C_4H_5)(C_6H_5)\end{matrix}\right\} NP.$$

Triethylphosphine has remained in contact with sulphocyanide of ethyle for more than a month without depositing any crystals. *A priori*, however, the formation of an urea under these circumstances was doubtful, since sulphocyanide of ethyle differs from the corresponding phenyle- and allyle-compounds, even in its deportment with ammonia and the monamines.

In concusion, it deserves to be mentioned that there appears to exist a similar series of arseniuretted ureas. Triethylarsine, when left for some weeks in contact with sulphocyanide of phenyle, deposits small crystals of a body which I believe to be the arsenic-compound corresponding to the phosphorus-urea described in this paper. This body requires a more minute examination.

* Proceedings of the Royal Society, vol. ix. p. 276. † Ibid. p. 290.

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On Solutions of Sesquisalts of Manganese. By H. Rose.

Sesquioxide of manganese is a very weak base, which is separated from many of its saline compounds in the form of hydrate, even by water. As Carius has shown, sesquioxide of manganese only dissolves in an excess of sulphuric acid when it contains protoxide; it then furnishes a purple-red solution.

From the solution of this double salt the sesquioxide of manganese is only thrown down by a large quantity of water, in consequence of the great amount of free acid. The precipitation is complete, and the filtered solution contains only protoxide of manganese.

The solutions of sesquioxide of manganese in oxyacids have so close a resemblance to a solution of permanganate of potash, that this oxide in them has frequently been regarded as a modification of permanganic acid. The solution of the sesquiphosphate of manganese exhibits the most remarkable behaviour.

If sesquioxide, proto-peroxide, or peroxide of manganese, manganates, or permanganates be heated with syrupous phosphoric acid, they dissolve in it. When the heat is continued until the acid begins to be volatilized a little, the mass, while hot, has a fine deep blue colour, like that communicated to fluxes by oxide of cobalt. On cooling, the mass becomes of a beautiful purple colour; with water it furnishes a solution of the same colour, exactly similar to a solution of permanganate of potash. It, however, contains sesquioxide of manganese, which is protected from precipitation by water by the phosphoric acid, by which it acquires a great stability, is not decomposed even by long boiling, and exhibits a different behaviour towards reagents in general, as indeed phosphoric acid usually acts in this respect upon many metallic oxides in the same way as tartaric acid and other organic acids. Hydrate of potash produces a brown precipitate in the solution; the supernatant fluid is colourless.

If a solution of oxide of chromium in an excess of hydrate of potash prepared at the ordinary temperature be added to the solution, brown sesquioxide of manganese is thrown down; the filtered fluid is colourless, not yellow, and contains no trace of chromate of potash; it could not consequently contain any permanganic acid. Ammonia produces no precipitate in the solution, to which, however, it gives a deep brown colour, and the solution remains clear even after dilution with much water. In this solution sulphuret of ammonium produces no precipitate of sulphuret of manganese. A solution of carbonate of soda gives a pale brown precipitate, but the supernatant fluid remains of a brown colour. In this, sulphuret of manganese is produced by sulphuret of ammonium by long action. If, after the saturation of the red fluid with carbonate of soda, a solution of cyanide of potassium be added to it, a clear brown solution is obtained in which no sulphuret of manganese is produced by sulphuret of ammonium.

Oxalic acid immediately renders the red solution brown, and in course of time quite colourless. If muriatic acid be added to the rather concentrated red solution, the latter becomes dark brown, and acquires the colour of perchloride of manganese; but if it be diluted with water, it again becomes purple. The solution is not decolorized by the action of muriatic acid; even after long heating the colour of the solution only becomes a little lighter. Even when alcohol is added, long-continued heat and time are necessary to produce decolorization. The presence of phosphoric acid therefore long hinders the deoxidation of the sesquioxide of manganese by muriatic acid. But the decolorization takes place rapidly when muriatic acid and a little sugar are added to the solution and heat is then applied.

Nitric acid, containing even but a small quantity of nitrous acid, decolorizes the solution immediately.

By carbonate of baryta the red solution is immediately decolorized even at ordinary temperatures; red sesquiphosphate of manganese is thrown down. The filtered solution contains no fixed constituents. The red precipitate dissolves in acids with a purple-red colour, and exhibits its original properties after the baryta has been got rid of by sulphuric acid.

Ferrocyanide of potassium produces a greenish, and ferridcyanide a brown precipitate, as in a solution of perchloride of manganese.

Deceptive as is the similarity in point of colour of the solution of sesquiphosphate of manganese with that of permanganate of potash, there is nevertheless a slight difference when the two solutions are looked at by lamplight, or by daylight when diluted with a large quantity of water. In both cases the permanganate of potash retains its purple colour; the solution of the sesquiphosphate, on the contrary, loses its violet tinge, and becomes more of a pure red colour.

If the solution of the sesquioxide of manganese in syrupous phosphoric acid be more strongly heated, it is decolorized, and contains protoxide of manganese. When the quantity of sesquioxide of manganese is considerable, a long fusion is necessary for this purpose; but the decolorization is more rapidly effected when the syrup is

heated in the platinum vessel to so strong a red heat that it begins to boil. If a little nitrate or chlorate of potash be added to the colourless mass and the whole be gently heated, it again becomes blue, and on cooling purple.

If protoxide of manganese or one of its salts be fused with syrupous phosphoric acid, a colourless clear mass is obtained which dissolves completely in water. The smallest quantities of sesquioxide, or of a higher grade of oxidation in the protoxide, colours the mass purple-red.

In the colourless solution hydrate of potash at first produces no alteration, but by degrees the fluid becomes brown from the surface downwards, and at last a brown precipitate of hydrated sesquioxide of manganese is deposited. This takes place more rapidly on the application of heat. Ammonia leaves the solution entirely unchanged; even after a long time no formation of hydrated sesquioxide of manganese takes place. If it be heated, a white precipitate of metaphosphate of protoxide of manganese is formed; this does not dissolve in much water. No precipitate of sulphuret of manganese is produced in the ammoniacal solution by sulphuret of ammonium; nor does nitrate of silver produce a black precipitate of the compound of sesquioxide of manganese and protoxide of silver. Ferrocyanide and ferridcyanide of potassium behave with the solution as with other solutions of protoxide of manganese. Carbonate of baryta completely precipitates the metaphosphate of protoxide of manganese from the solution at ordinary temperatures. If the precipitate be dissolved in muriatic acid, and the baryta removed by sulphuric acid, the precipitate produced in the solution by hydrate of potash very soon becomes brown; ammonia throws down a white precipitate even at ordinary temperatures, but this is not converted into sulphuret of manganese by sulphuret of ammonium.

When protoxide of manganese has been dissolved in syrupous phosphoric acid by the aid of heat, the colourless mass becomes purple if it be gently heated for a long time with access of air, but so that it does not begin to volatilize. In this way, however, it can only acquire a slight and pale purple colour. Here, therefore, similar phænomena are manifested, as when bodies containing manganese are dissolved in phosphorus salt by the blowpipe flame. In the external flame the globule is of an amethyst colour, but far less strongly than in borax-glass; in the inner flame it becomes colourless, and this result is produced less by the reducing gases of the blowpipe, than by the mere action of the high temperature with exclusion of air.

The solution of perchloride of manganese does not share the purple colour of the solutions of the oxysalts of the sesquioxide. It is of a deep blackish-brown colour. Towards reagents, however, the solution of the perchloride and that of the sesquisulphate (containing protoxide) behave nearly in the same way. From both, sesquioxide is thrown down in the form of hydrate by the agency of water. Some protochloride also is always contained in the blackish-brown solution of the perchloride. If syrupous phosphoric acid be

added to a somewhat concentrated solution of perchloride of manganese, no change is produced; but if the whole be diluted with water, it gives a purple-red colour.

Walter Crum has described a method of detecting the smallest quantities of protoxide of manganese in a solution. It consists in heating brown superoxide of lead with dilute nitric acid, and adding to this a small quantity of the solution. When protoxide of manganese is present, the fluid acquires an intense purple-red colour, which is very easily recognized when the excess of the superoxide has settled to the bottom. This test is indeed of surprising sensitiveness, and certainly the most sensitive we have for manganese in the humid way. The purple colour of the solution does not, however, arise from permanganic acid, but from sesquioxide of manganese. By many methods which have been given for the preparation of permanganic acid also, only a solution of sesquioxide of manganese is obtained.—Poggendorff's *Annalen*, vol. cv. p. 289.

On Fibroine and the Horny Substance of Sponge.
By J. Schlossberger.

The organic substance of the common sponge was declared by Crookewit, in consequence of the results of elementary analyses, to be identical with the fibroine of silk threads. In Crookewit's opinion the fibroine of the sponge is combined with small quantities of iodine, sulphur, and phosphorus which are wanting in silk. The author has already (in his 'Vergleichende Thierchemie') expressed doubts of the correctness of this view, and now publishes the following observations upon the behaviour of these substances to the remarkable solvents, ammoniacal solutions of oxide of copper and of protoxide of nickel.

In these solvents, silk, whether in the raw state or boiled, swells up remarkably rapidly and strongly, and soon dissolves; the colour of the solution of silk is blue with a violet tinge with $CuO\,NH^3$, and yellowish brown with $NiO\,NH^3$. The common sponge, on the contrary, undergoes no corresponding change in either of the reagents, even when they are employed perfectly fresh, and saturated as much as possible with the heavy metallic oxides; even after lying in them for six weeks, no swelling of the sponge-fibres could be detected either by the naked eye or the microscope; the only change in the solution of nickel was that this had in part lost its blue colour, and the sponge had become reddish brown.

To prevent the solubility of the sponge from being diminished by the salts contained in it, the author purified it as much as possible by mechanical means and by extraction with dilute nitric acid. The purified sponge, however, always left 4·66 per cent. of ash, containing 0·72 of soluble, and 3·94 of insoluble constituents.

In consequence of this, the author felt still more doubt as to the correctness of the supposition that the substance of the sponge is fibroine, although he admits it to be possible that the small quantities of iodine, sulphur, and phosphorus, which, according to Crooke-

wit, are chemically combined with the substance of the sponge, may prevent its solubility. The author convinced himself that clean-washed sponge, after combustion with potash and nitrate of potash, leaves phosphoric acid, sulphuric acid, and iodine in the ash.

He also found iodine in the ash of the skeleton of the *Gorgoniæ*, after it had been thoroughly washed with water and muriatic acid.

The web of the indigenous *Bombicidæ* behaves to the two solvents $CuO\,NH^3$ and $NiO\,NH^3$ exactly in the same way as that of the silkworm; the fibres swell up strongly, and soon become invisible in consequence of their dissolving. Further, solutions of oxide of copper or protoxide of nickel in carbonate of ammonia have no action upon silk; towards cotton also they are both destitute of action. This explains why the solutions of these oxides in ammonia lose so much of their solvent power by long keeping, even when strong ammonia is again added to them before they are made use of. —Liebig's *Annalen*, cviii. p. 62.

New Method of preparing Sulphurous Acid. By E. F. Anthon.

There are various methods of preparing sulphurous acid, of which, however, those only are usually employed which depend on the combustion of sulphur (or iron pyrites), or upon the decomposition of heated concentrated sulphuric acid by sawdust and the like, or by metals.

The first of these methods is certainly simple and cheap, but it is not applicable in many cases. The decomposition of sulphuric acid by copper or mercury is expensive, and also presents other inconveniences. The decomposition of sulphuric acid by chips of wood and other organic matters is also expensive, because in consequence of their great volume, a great excess of sulphuric acid must be employed, which escapes decomposition. Moreover, the sulphurous acid thus obtained is contaminated with more or less carbonic acid.

(The preparation of sulphurous acid by decomposition with charcoal, which is easily effected, is passed over by the author, and consequently the question is left unanswered, whether the preparation of sulphurous acid by boiling sulphuric acid with sulphur is more convenient than this. It appears from the original that the fact that sulphuric acid is decomposed by boiling with sulphur is unknown to the author, and yet it is now indicated in the Chemical Textbooks. The method described by the author is consequently not new, and therefore only deserves further notice, if it be more convenient for the preparation of sulphurous acid than it was supposed to be.—Ed. *Chem. Centralblatt.*)

The author placed

2 ounces of sulphur in fragments, and
25 ounces of concentrated sulphuric acid

into a glass flask, furnished with a gas-tube, and heated it over a spirit-lamp. The sulphur soon melted, and in a short time there

was an evolution of sulphurous acid which was conducted into water. The evolution was very uniform, and the burning of the spirit-lamp was continued until, after about six hours, there was only a comparatively small residue in the flask.

During this treatment the sulphur constantly floated in the form of a transparent, hyacinth-red, thickly fluid mass on the hot sulphuric acid, and a small portion of it sublimed; part of this condensed again in drops upon the walls of the flask, and flowed back into the acid, whilst another part was deposited in the form of a thin crust in the neck of the flask. Very small quantities of sulphur were carried further mechanically by the sulphurous acid, and deposited in the conducting-tube, and the water placed to absorb the gas.

After the conclusion of the process the flask contained only

4½ drachms of sulphuric acid, and
32 grains of unaltered sulphur.

The advantages of this process are:—

1. That it furnishes a pure product;
2. That it is easily effected, and cheap;
3. That the evolution of sulphurous acid gas is very uniform, the reason of which is that the sulphuric acid always acts only upon the outer surface of the melted sulphur, and this always forms a coherent mass; and
4. That no solid deposit settles to the bottom of the vessel of evolution, which, in other methods, so often occasions the cracking of the vessel.—Dingler's *Polyt. Journal*, cl. p. 379; and *Chem. Centralblatt*, Feb. 2, 1859, p. 78.

Preparation of Molybdate of Ammonia. *By* C. Brunner.

Since the employment of this salt for the detection of phosphoric acid has become indispensable in chemical analyses, several methods have been recommended for its preparation. Most of these start from the roasting of native sulphuret of molybdenum in contact with the air, until all the sulphur is burnt away and the molybdenum is converted into molybdic acid, which is afterwards dissolved in ammonia; this operation is usually carried on in an obliquely placed platinum crucible, the mass being frequently stirred, but it is very tedious. The improvement of this method lately described by Wöhler, in which a draught of air produced by an aspirator is employed, also effects the object but slowly. The reason of this is to be found partly in the difficulty of dividing the material sufficiently, as it always cakes together again when heated, and partly in the fact that the molybdic acid produced covers the residue of the mineral and thus renders its ignition difficult.

The operation may be effected very easily in the following way:—The sulphuret of molybdenum is triturated in an agate mortar with about an equal volume of coarse quartz-sand washed with muriatic acid until it forms a moderately fine powder, which is placed in a shallow platinum cup or on platinum foil, and heated over a good

spirit-lamp to the commencement of incandescence, stirring it frequently until the mixture has acquired a citron-yellow colour (whitish, on cooling). A quarter of an hour is sufficient to effect this with several grammes of the mixture. When cool, the mass is extracted with liquid ammonia and further treated in the usual way. —Dingler's *Polyt. Journal*, cl. p. 372.

On Bryonia alba. *By* G. F. Walz.

The author first prepared an extract of the root of *Bryonia* with alcohol of spec. grav. 0·830, distilled the alcohol off and dried the residue. This residue is partly soluble, partly insoluble in water.

The portion soluble in water contains bryonine, bryonitine, a yellow resin soluble in æther, brown fat, and a colouring matter which is soluble in water and alcohol.

The insoluble portion contains but little bryonine, bryonitine, yellow resin soluble in æther and brown fat, together with a colouring matter soluble in alcohol.

1. *The portion soluble in water.*—The aqueous solution is of a reddish-yellow colour and an acrid bitter taste; when mixed with acetate of lead only a slight turbidity was produced, but with basic acetate of lead a strong precipitate of a yellow colour is formed. The entire aqueous fluid was completely precipitated with basic acetate of lead; the precipitate was well washed with water, and decomposed by sulphuretted hydrogen.

The aqueous fluid standing over the sulphuret of lead was of a brownish-yellow colour, and of a strong bitter taste. It was carefully evaporated to dryness, by which means all acetic acid was removed, and a brown mass remained. This was treated with absolute æther, which acquired a strong reddish-brown colour, and dissolved the greater part of it. After the æther was distilled off, a crumbly mass remained; a portion of this dissolved with a reddish-brown colour, whilst the other, consisting of bryonitine, remained in small white crystals. The residue, insoluble in æther, was only partially soluble in water; the solution was reddish brown, and had a strongly bitter taste. It was further examined, and consisted of gum, reddish-brown colouring matter, and bryonine. These three substances were separated by precipitating the colouring matter first of all with acetate of lead, the gum with basic acetate of lead, and the bryonine, from the fluid when freed from oxide of lead, by tannine. Some bryonitine still adhered to the bryonine; it was removed by æther.

The sulphuret of lead obtained by the decomposition of the precipitate formed with basic acetate of lead, was completely extracted with alcohol; it furnished a brownish-red tincture of a bitter taste. On evaporation, this left a brown and very brittle mass, which furnished nothing to æther, but dissolved in absolute alcohol without any residue. On the addition of an alcoholic solution of acetate of lead no turbidity was produced; when the alcohol was evaporated, it left a shining brown, readily triturable mass.

From the fluid filtered from the precipitate formed by basic acetate of lead, the lead was thrown down by sulphuretted hydrogen, the sulphuret of lead was well washed, dried, and extracted with alcohol. A dark brownish-red tincture was obtained. After the removal of the alcohol, there remained a few drachms of a tenacious residue. This was dissolved in absolute alcohol, when flakes separated, which proved to be gum with a little colouring matter and traces of bryonitine. It was again evaporated to dryness, and a similar residue was obtained. Æther extracted a portion of this; after the æther was distilled off, there remained a brown mass, insoluble in water, which dissolved almost entirely in absolute alcohol, depositing a little bryonitine. The portion insoluble in æther was only partially taken up by water; a brown portion, insoluble in alcohol, remained. This was not precipitated by alcoholic solution of acetate of lead; on evaporation, the above-mentioned slimy brown body remained.

The dark brownish-red portion, soluble in water, had a strong bitter taste; it contained various substances; the brown colouring matter soluble in water was precipitated by acetate of lead; basic acetate of lead also produced a strong precipitate; this, after decomposition, still contained gum and a little colouring matter, and in the fluid filtered from the precipitate formed by basic acetate of lead, there was much bryonine, from which æther extracted a little bryonitine.

Those portions of the part soluble in æther from which the bryonitine had been precipitated by absolute alcohol, were mixed from both operations; they formed a reddish-brown tincture of bitter taste, but became strongly turbid by alcoholic solution of acetate of lead. They were precipitated therewith; the precipitate, when decomposed, furnished a peculiar fatty body, whilst the solution, when evaporated, left a yellowish-red substance of a bitter taste and resinous aspect.

The bryonitine obtained from the different portions was then dissolved in æther, and digested with animal charcoal; the decolorization only took place slowly; when the æther was distilled off, white crusts made their appearance on the walls of the retort, and after the greater part had been expelled, and the contents of the retort solidified on cooling, a white, granular, gelatinous mass, consisting of fine crystals, had been formed, whilst a brown resin was deposited at the bottom. On the addition of boiling water, the crystals dissolved, leaving the above-mentioned brown bitter resin. Pure bryonitine crystallized from the aqueous solution.

The original aqueous solution from which the oxide of lead had been thrown down by sulphuretted hydrogen, was of a light wine-yellow colour, and of a very bitter taste; it was mixed with a pure aqueous solution of tannine as long as a precipitate was produced. The fluid was heated, and the precipitate contracted very rapidly into a shining resinous mass. The decanted acid fluid, when neutralized by carbonate of soda, gave another precipitate, which, however, did not so readily contract into a resin. The perfectly neutral

fluid, filtered from the flakes produced, contained an excess of tannine with bitter extractive matter.

To remove the former, the fluid was precipitated with basic acetate of lead, the excess of lead removed by sulphuretted hydrogen, and the fluid exactly neutralized with soda, and carefully evaporated to dryness. There remained a very bitter extract; this was first of all digested with absolute æther in order to test it for bryonitine; only traces were left after the evaporation of the æther. The portion remaining undissolved contained some gum and sugar, together with bryonine, which was the cause of the bitter taste.

The tannic precipitate was dissolved as a resinous mass in alcohol, and mixed, for experiment, with caustic lime suspended in alcohol; after digesting for several hours, all the tannine was removed from the fluid, but the latter had acquired a bright red colour, with a tinge of violet. The alcoholic solution was again digested for some days with pure animal charcoal, without losing its colour.

The greater part of the alcohol was distilled off, and the rest got rid of by spontaneous evaporation; there remained a granular, reddish-white mass, transparent in thin layers, stable in the air, and free from any ash. The nearly pure bryonine was digested with absolute æther, and constantly agitated as long as any of it was dissolved. After the evaporation of the æther, there remained the bitter resin so often mentioned. To deprive the bryonine of the reddish colour produced by lime, it had to be repeatedly dissolved in water, precipitated by tannine, and decomposed by means of oxide of lead.

The bryonine freed from all impurity by this means was again dissolved in water, and digested with pure animal charcoal; the solution, which had very little colour, lost it entirely and left pure bryonine on evaporation. Analyses of bryonine gave:—

C	59·91	96	60·00
H	8·37	80	8·33
O	31·72	38	31·66

2. *The resinous residue left undissolved by water.*—This was dissolved in absolute alcohol. In this way some impure bryonitine remains; this was purified by washing with absolute alcohol, solution in æther, and decolorization of this solution by animal charcoal; and after it was prepared in a solid state by distilling off the æther, it was recrystallized from water, when it was perfectly pure.

The alcoholic solution, filtered from the above residue, was also digested with animal charcoal, but was only slightly decolorized by this means. After the alcohol had been distilled off and the residue evaporated, a brown, somewhat granular mass remained; this was for the most part soluble in æther, leaving a very dark-coloured substance. The latter was soluble in ordinary alcohol, but was rendered strongly turbid by an alcoholic solution of acetate of lead; it was completely precipitated therewith, the excess of oxide of lead was removed from the fluid by sulphuretted hydrogen, and the fluid, after filtration, was then left to spontaneous evaporation; there

remained an amorphous, very bitter, shining, brown mass. The lead precipitate parted with very little to water after decomposition by sulphuretted hydrogen; alcohol, on the contrary, extracted a dark brown amorphous body from the sulphuret of lead. Animal charcoal also extracted very little colour from the ætherial extract; the æther was distilled off, the residue evaporated to dryness, and again dissolved in absolute alcohol; flakes again separated which contained bryonitine.

Acetate of lead dissolved in alcohol produced strong turbidity with a precipitate in the alcoholic solution; the fluid was precipitated, the excess of oxide of lead removed with sulphuretted hydrogen, and it was again evaporated. The residue, which contained much acetic acid from the acetate of lead, required to be frequently washed in order to remove this; only a very little bitter matter was extracted. The residue, when freed from acid, solidified into a reddish-brown mass of peculiar odour. In order to ascertain the properties of this body, it was first of all dissolved in absolute alcohol; during its solution very fine glistening crystals separated in abundance, but when the mixture was slightly heated, the crystals disappeared, and did not again separate on cooling; a further dilution with absolute alcohol also caused no fresh separation.

The alcohol, therefore, had to be evaporated again and the residue redissolved in cold absolute alcohol. The crystals then separated again; they were collected by filtration and added to the stock of bryonitine. The alcoholic solution, evaporated to dryness, left behind a mass which was but little altered.

The lead precipitate produced in the alcoholic solution was decomposed by sulphuretted hydrogen; water took up very little from it, but alcohol acquired a brownish-red colour and, when evaporated, left a brown fatty mass of a peculiar odour, but without any bitterness, which was still soft at 32° F.

Bryonine, when boiled with dilute sulphuric acid, splits into sugar and two other amorphous bodies, which are insoluble in water; one of these, bryoretine, is soluble, and the other, hydrobryoretine, insoluble in æther. Analyses of bryoretine gave—

C	63·09	42	63·13
H	8·78	35	8·77
O	28·13	14	28·10

The product insoluble in æther, hydrobryoretine, dissolves in alcohol, and is considerably decolorized by animal charcoal; it solidifies, on the evaporation of the alcohol, into a clear amorphous mass, and furnishes on combustion the following results:—

C	60·00	42	60·43
H	9·36	37	8·87
O	30·64	16	30·70

This body differs from bryoretine by containing 2 atoms more water.

The author therefore concludes that bryonine splits into sugar, bryoretine, and hydrobryoretine in the following manner:—

$$C^{56}H^{84}O^{42} = C^{42}H^{35}O^{14} + C^{42}H^{37}O^{16} + C^{12}H^{12}O^{12}.$$

The sugar was determined by means of Fehling's fluid in the liquid from which the bryoretine and hydrobryoretine had been deposited.—*Archiv der Pharmacie*, cxlvi. p. 150.

On the Isomeric Modifications of Peroxide of Tin. *By* H. Rose.

In a previous memoir the author has fully detailed the essential differences between the two isomeric modifications of peroxide of tin. Besides the reactions there referred to, they are strikingly distinguished when dissolved in muriatic acid by their different behaviour when distilled.

If an aqueous solution of perchloride of tin, or of crystallized hydrate of perchloride of tin, be distilled, some muriatic acid is certainly evolved, first of all with the aqueous vapour, but afterwards muriatic acid and peroxide of tin pass over together, or rather perchloride of tin is volatilized together with the aqueous vapour, and some peroxide of tin remains. Even by an addition of concentrated sulphuric acid the volatilization of the perchloride of tin cannot be prevented, nor can it be decomposed. If it be evaporated until the sulphuric acid begins to volatilize, its vapours are accompanied by anhydrous perchloride of tin, and there remains a little sulphate of tin, which may be dissolved in a little water by long contact therewith. Even the addition of nitric acid is incapable of preventing the volatilization of perchloride of tin. Perchloride of tin and nitric acid are volatilized with the aqueous vapours; when the residue is strongly heated, anhydrous perchloride of tin passes over and peroxide of tin is left.

If, on the other hand, the muriatic acid solution of the *b*-peroxide of tin, obtained by means of nitric acid and metallic tin, and freed from all nitric acid by washing with water, be distilled, it is rendered turbid by the heat; muriatic acid alone distils over without any peroxide of tin, and it is only at last, when the residue in the retort has become nearly dry, that a little perchloride of tin is formed, and distils over. Even when the solution has been mixed with much muriatic acid, it behaves in the same manner. If the muriatic solution of the *b*-peroxide be mixed with concentrated sulphuric acid, by which a dense precipitate is immediately produced, and then distilled, only muriatic acid, and finally sulphuric acid passes over, and sulphate of tin remains. Even with an addition of nitric acid, by which the muriatic solution of the *b*-peroxide is rendered turbid, no peroxide of tin is volatilized as perchloride of tin during distillation; it is only when the residue in the retort becomes very thick, that a small quantity of perchloride of tin is formed.

From this different behaviour of solutions of perchloride of tin and that of the peroxide *b* in muriatic acid, when submitted to distillation, it appears that in the latter the muriatic acid and peroxide

of tin do not combine to form a chloride. The difference between the two solutions therefore probably consists essentially in that the one contains true chloride, and the other permuriate of tin; and the distinction between the two modifications of peroxide of tin is to be found in the fact, that when they are separated from different solutions, they either form perchloride or permuriate immediately on their solution in muriatic acid.

The perchlorides and solutions of the peroxides of other metals in muriatic acid do not behave under distillation in so peculiar a manner as the compounds of tin.

If peroxide of antimony or sulphuret of antimony be dissolved in muriatic acid and the solution distilled, muriatic acid first of all passes over with the aqueous vapour, but subsequently perchloride of antimony, and lastly anhydrous perchloride. If nitric acid be added to the solution in muriatic acid, muriatic and nitric acids escape during the distillation, but no antimony; only, at last, when no more nitric acid is evolved, a very small quantity of the superchloride $Sb^2 Cl^{10}$ distils over, depositing itself in part in the form of solid crystalline hydrate, and being in part decomposed with evolution of chlorine under the influence of the heat, to form perchloride of antimony, $Sb^2 Cl^6$.

From a solution of arsenious acid in muriatic acid, perchloride of arsenic is volatilized when the solution begins to get concentrated; no residue remains in the retort. If concentrated sulphuric acid be added to such a solution, much perchloride of arsenic is volatilized from the very commencement of the distillation, and continues to pass until the sulphuric acid begins to be volatilized; the residue of sulphuric acid, however, still contains considerable quantities of arsenious acid.

If an aqueous solution of arsenious acid be mixed with nitric acid and distilled, the distillate contains no arsenic, which remains in the retort in the form of arsenic acid. The result is the same when nitric acid is added to a solution of arsenious acid in muriatic acid and the whole is distilled. Moreover, when chlorate of potash and muriatic acid are added to an aqueous solution of arsenious acid, or when chlorine gas is passed through a solution of arsenious acid in muriatic acid, and the solutions are submitted to distillation, no arsenic occurs in the distillate, except traces which have been carried over by the spirting. If a solution of arsenious acid mixed with muriatic acid be distilled, there is no arsenic in the distillate, and it is only at the end that traces of perchloride of arsenic pass over; the result is the same when concentrated sulphuric acid is added to a solution of arsenic acid in muriatic acid.

As in judicial investigations the arsenic in organic substances poisoned with arsenic is frequently obtained by distillation in the form of perchloride of arsenic, the author describes the precautions in detail which must be observed in order to volatilize all the arsenic in the form of perchloride, even when this exists in the organic substance as arsenic acid.—*Bericht der Akad. der Wiss. zu Berlin*, 1858, p. 621.

On the Behaviour of Ammonia towards Sulphur.
By C. Brunner.

If pure sulphur be digested with liquid ammonia, no action is detected even after a long time, when the temperature does not exceed 167° F. But if the fluid be more strongly heated, say to 189° F., it acquires a slight yellowish colour, which appears still more distinctly when boiled. A very small quantity of sulphur is then dissolved, for the fluid gives a brownish-red precipitate with acetate of lead. It contains no sulphuric acid. If a sample be saturated with muriatic acid, and the slight precipitate of sulphur be separated by filtration, chloride of barium does not produce the slightest turbidity even by long standing.

In a well-stoppered bottle the solution of sulphur in ammonia may be preserved without change. Even after being kept for some weeks, it still retains a yellowish colour and remains perfectly clear; it also furnishes the reddish precipitate with solution of lead. When exposed to the air it soon becomes turbid, and in twenty-four hours a slight precipitate of sulphur is formed. The solution filtered from this, furnishes a white precipitate with solution of lead, and with chloride of barium, a very slight reaction of sulphuric acid.

If the same sulphur be boiled repeatedly with ammonia, it acquires a pale colour, with somewhat of a greyish tinge. If this be repeated until the greater part of the sulphur is dissolved, there remains a flocculent greyish-black residue, which disappears entirely when heated with bichromate of potash and sulphuric acid. This is evidently a little carbon, which appears to be present in all sulphur, even when it is purified by three or four distillations.—Dingler's *Polyt. Journal*, cl. p. 371.

On a New Colouring Matter in the Fruits of Paulownia imperialis.
By M. Belhomme.

The author has sent to the Academy of Sciences of Paris a sample of a crystallized, yellow colouring matter, obtained from the capsules of *Paulownia imperialis*. He calls it paulownic acid.—*Comptes Rendus*, xlvii. p. 214.

ANALYTICAL CHEMISTRY.

On the Separation of Zinc from Nickel. *By* Professor C. Brunner.

For the separation and quantitative determination of zinc and nickel several methods have lately been recommended. One of the simplest appears to be that described by Smith, which is founded on the circumstance, that from a solution of the two oxides in acetic acid only the zinc is thrown down by sulphuretted hydrogen gas. With regard to this process, Rose remarks that an exact separation can take place only when no strong acid is present in the solution.

Rammelsberg declares the method to be inexact, and says expressly that nickel is always precipitated with the zinc.

A series of experiments made upon this subject have led to a method of operation which appears to give a good result.

A solution of the two metals in muriatic or nitric acid is first made, and diluted until there are at least 500 grms. of fluid to every gramme of the two oxides, and this solution is approximatively saturated with carbonate of soda, so that only a very small quantity of free acid remains In order to hit this point accurately, a dilute solution of the soda-salt is added until, after some shaking and standing, the precipitate does not entirely disappear, when it is taken up by a few drops of acid. Sulphuretted hydrogen gas is then passed through the fluid, by which, after some time, a perfectly white precipitate (sulphuret of zinc) is produced. After a good portion of zinc has thus been thrown down, a few drops of very dilute solution of acetate of soda are added to it, and the passage of sulphuretted hydrogen is continued as long as the precipitate appears to increase; the vessel is then allowed to stand 10 or 12 hours at the ordinary temperature. The precipitate settles completely, and may easily be washed on a filter.

To make sure that all the zinc is thrown down, a sample of the filtered fluid is mixed with one drop of dilute solution of acetate of soda, and treated with sulphuretted hydrogen. If a whitish turbidity be produced, the whole fluid must be treated in the same way.

From the fluid thus freed from zinc, the nickel may now be thrown down (after the expulsion of the sulphuretted hydrogen by heat) by means of hydrate of potash. The precipitate of sulphuret of zinc, after being sufficiently washed, is placed with the filter in a glass, and digested with muriatic acid until all odour of sulphuretted hydrogen has disappeared; the solution diluted with water is then filtered, and the zinc determined by the known methods.

In this separation the acetate of soda evidently plays an auxiliary part. A small quantitity of acetate of zinc is formed by mutual decomposition, and this is precipitated by sulphuretted hydrogen. The acetic acid set free forms acetate of zinc again, and this is also immediately precipitated. The action may be compared with the formation of carbonate of lead by the action of carbonic acid gas upon a mixture of litharge and acetate of lead stirred up with water. Hence it is intelligible how so small a quantity of acetate of soda is necessary.

In order that the separation may be exact and that no nickel may be precipitated with the zinc, the following precautions are to be observed:—

1. The solution must at first be slightly, but not too weakly acid, —containing about 1 or 2 drops of free acid. If it be perfectly neutral, the precipitate appears of a dingy colour, and contains nickel. When the proportion is accurately observed it is pure white. After washing, nickel cannot be detected in it, either by the blowpipe or by any other means.

2. Too great an amount of acetate of soda, and any heating must

also be avoided. Thus if a considerable quantity of acetate of soda be added, some nickel is thrown down,—indeed by this means, especially when heat is applied at the same time, all the nickel may be completely precipitated.

In experiments with accurately weighed portions of the oxides (0·2 to 0·3 grm. of each) they were reproduced within 1 or 2 milligrms.

Zinc may be separated from cobalt in the same way. The sulphuret of zinc deposited from a solution containing cobalt, always gave an oxide which produced no colour when heated before the blowpipe with borax.

Lastly, it is to be observed that, when iron is present, it must be previously separated, as otherwise it passes partly into the zinc and partly into the nickel precipitate. The best method in this case is that of Fuchs with carbonate of baryta, and subsequent removal of the baryta by sulphuric acid. The separation by ammonia is not applicable, as by it the subsequent separation of the two metals is rendered impossible.—Dingler's *Polyt. Journal*, cl. p. 369.

Quantitative Determination of the Amount of Tannine in Tanning Materials. *By* Gustav Müller.

The precipitant employed by the author for the determination of the tannine in fluids is a solution of gelatine, which has already been made use of for the same purpose; but the author has convinced himself by numerous experiments, that an accurate determination of tannine by means of solution of gelatine cannot be made directly, inasmuch as the yellowish-brown precipitate of gelatine containing tannine, or tannate of gelatine, thus produced is never so completely separated from the solution that the supernatant fluid remains perfectly clear, which, however, must be the case if the precipitation of the tannine by solution of gelatine be adopted for the quantitative determination of the tannine in fluids.

After many trials, the author found that the addition of a small quantity of alum to the solution of gelatine furnished a suitable means to enable tannine to be precipitated without any difficulty from any fluids containing it, so that it might be determined with the greatest exactitude; the separation of the precipitate (tannate) takes place so rapidly and completely that in the course of a few minutes the fluid over the precipitate appears quite limpid, and consequently may be immediately tested for any possible residue of tannine. For this purpose, according to the author, the best plan is to employ two watch-glasses, placed upon a black ground to enable the reaction to be detected with more ease; a few drops of the fluid standing over the precipitate are taken up with a little stick and dropped into each watch-glass, and then into one glass two drops of the aluminous solution of gelatine, and into the other a drop of solution of tannine or decoction of galls; a distinct rod should be used for each test-fluid in order to avoid mistakes. In this way, by the turbidity produced, we may detect on the one hand the smallest quantities of tannine, and on the other, the smallest traces of gelatine, in case the quantity necessary for precipitation should have been exceeded. To

avoid the latter occurrence, the solution of gelatine is only dropped into the solution of tannine under examination, but this is continued uninterruptedly until on the falling of a drop upon the surface, the characteristic ring of tannate of gelatine is no more to be detected. When this moment occurs, it is necessary that the precipitation should be interrupted for a time, and that the fluid, which appears limpid after the lapse of a few minutes, should be tested for tannine. The little trouble attending this operation should not prevent its being done frequently, in order that no more of the aluminous solution of gelatine may be employed than is just necessary for the precipitation of the tannine, as the amount of the latter is finally calculated from that of the gelatine.

In order to ascertain how much aluminous solution of gelatine represents a given quantity of pure tannine, 5 grs. of the latter were dissolved in half an ounce of distilled water, and precipitated with the greatest care. After repeating the experiment five times, the author found that 155 grs. of the solution of gelatine were required for this purpose. Consequently a decoction of $\frac{1}{4}$ ounce of oak-bark, if 1 ounce (=480 grs.) of aluminous solution of gelatine were employed in its precipitation, would have contained $15\frac{1}{31}$ grs. of tannine, in accordance with the formula

$$155 : 5 \; : : \; 480 : 15\tfrac{1}{31}.$$

The quantity of solution of gelatine employed for the determination of tannine is ascertained by accurately weighing a 3 or 4 ounce glass filled with it, and ascertaining the difference of weight after the precipitation; this difference of course indicates the quantity of solution of gelatine employed.

For the preparation of the aluminous solution of gelatine, 4 ounces of distilled water are weighed in a phial; into this 1 drachm of ordinary clean joiner's glue, crushed a little, is put, when the glass, surrounded with paper, is placed in a vessel of water, and set upon the fire. When the glue is dissolved, which takes place without any residue when the so-called Russian glue is made use of, 15 grs. of pure powdered alum are added to the hot fluid, which is then shaken round several times, and may be kept, well-stoppered, in a dark place.

The substances (about 50—100 grs.), the amount of tannine in which is to be ascertained, are to be extracted for a few minutes with as much distilled water as will cover them; and this process must be repeated from four to six times, with constant stirring, so as to exhaust them as much as possible. The decoctions are poured off each time, without straining; the fluids, to which the residue is finally added, are collected in a beaker, but the determination of the tannine must not be proceeded with until they are cold. In dropping in the cold solution of gelatine, a small rod must be employed to prevent it from flowing out in a stream, by which, especially towards the close of the experiment, the precipitation might easily be exceeded. It is also well to allow the exhausted residue to remain in the fluid, as it assists greatly in the rapid separation of the tannate of gelatine.

The determinations effected by the author in the way above described gave the following results:—

	Grains of tannine.
100 grs. of young oak-bark	$13\frac{27}{31}$
„ „ of oak-bark from a tree 100 years old	$8\frac{14}{31}$
„ „ Eschurg oak-bark	$19\frac{11}{31}$
„ „ Pine-bark from young stems	$12\frac{28}{31}$
„ „ of native galls	$50\frac{1}{2}$
„ „ of Divi divi	$49\frac{8}{31}$
„ „ of Sumach	$19\frac{11}{31}$
„ „ of Tormentilla root	$31\frac{19}{31}$
„ „ of American bark (the so-called Mimosa-bark, probably belonging to a cinchonaceous plant)	$31\frac{5}{31}$
„ „ of best gall-nuts	$77\frac{13}{31}$
„ „ of Chinese galls (from *Rhus semi-alatum*)	$65\frac{25}{34}$

Elsner's *Technisch-chemische Mittheilungen* für 1857–1858, p. 45; *Polytechn. Centralblatt*, 1859, p. 56.

On the Qualitative Separation of the Oxides of Mercury, Lead, Bismuth, Copper, and Cadmium. *By* Julius Löwe.

A solution containing salts of mercury, lead, bismuth, copper, and cadmium is precipitated by sulphuretted hydrogen, or separated from tin, arsenic, antimony, &c., by sulphuret of ammonium (sulphuret of potassium); the washed metallic sulphurets are decomposed by concentrated nitric acid in a porcelain capsule, and the excess of acid evaporated on the water-bath. The residue is treated with a little water, and then again evaporated, and this process is repeated three or four times. After the last evaporation, the dry residue is left upon the hot water-bath until the black residue (sulphuret of mercury) no longer betrays any evolution of nitric acid by the odour, and all the nitrate of copper is converted into basic salt. The contents of the capsule are then allowed to cool, treated with a solution of 1 part of nitrate of ammonia in 500 parts of water, and filtered. When large quantities of oxide of lead are present, this solution remains colourless, with smaller quantities it becomes blue, because the sulphuric acid produced by the oxidation of the metallic sulphurets decomposes a portion of the basic copper-salt during the evaporation, and forms sulphate of copper. In this case one or two drops of a dilute solution of nitrate of baryta are added to the blue solution, which is then evaporated to remove the nitric acid of the neutral nitrate of copper thus formed, and convert it into basic salt. When the solution exhibits this blue colour, we may be convinced that no oxide of lead is to be detected in it by sulphuric acid, as the whole amount of oxide of lead present is already contained in the insoluble residue in the form of sulphate of lead, for otherwise the fluid could contain no free sulphuric acid, and no sulphate of copper could have been dissolved.

A. *Treatment of the filtrate.*—Dilute sulphuric acid in not too great excess is added to the fluid filtered from the insoluble basic

nitrates of bismuth and copper, sulphate of lead, and sulphuret of mercury. The production of a white precipitate, which when collected on a filter and repeatedly washed with water is blackened by sulphuret of ammonium, indicates the presence of oxide of lead. In the fluid filtered from the sulphate of lead the presence of oxide of cadmium is detected by the addition of solution of sulphuretted hydrogen, or by the passage of that gas through the solution, by the yellow precipitate thus produced. If the solution mixed with dilute sulphuric acid be evaporated to dryness on the water-bath until the nitric acid set free has been driven off, and the residue be treated with water and filtered, and the filtrate tested by sulphuretted hydrogen for oxide of cadmium, the precipitate of sulphuret of cadmium usually appears of a purer yellow colour, as the fluid thus obtained is free from small quantities of sulphate of lead, which are dissolved by the agency of the free nitric acid, and by afterwards forming sulphuret of lead, cause a discoloration of the sulphuret of cadmium.

B. *Treatment of the residue which is insoluble in Nitrate of Ammonia.*—Dilute nitric acid is poured over this, and filtered from the insoluble residue, which consists of sulphuret of mercury and sulphate of lead. The filtrate is divided into four portions, to the first of which a little muriatic acid and a large quantity of distilled water is added. Turbidity of the fluid indicates oxide of bismuth. If the solution contains too much free nitric acid, it is as well to neutralize this partially with a little caustic ammonia before the addition of the water. The second portion is mixed with a solution of neutral chromate of potash in excess; the formation of a light yellow precipitate, which forms a clear solution on the addition of a large quantity of nitric acid, also indicates oxide of bismuth. In carrying out this reaction it is also advisable to partially neutralize the excess of free nitric acid by a solution of carbonate of potash before the addition of the neutral chromate of potash, or in other cases, as stated above, to employ the chromate in excess, as otherwise the chromate of bismuth formed remains in solution in the excess of acid. The third portion is mixed with caustic ammonia until the production of an alkaline reaction; the production of a white precipitate and a blue solution indicates the presence of bismuth and copper by a single reaction. However, if the quantity of oxide of copper present be very small, so that there is a doubt as to the blue coloration of the ammoniacal solution, the fourth portion is treated with a solution of ferrocyanide of potassium, when a red-brown precipitate or a reddening of the fluid, renders the presence of copper a matter of certainty.

The residue insoluble in nitric acid, consisting of sulphuret of mercury and sulphate of lead, is repeatedly washed with dilute nitric acid, and finally with water, and then treated with a moderately concentrated cold solution of hyposulphite of soda; after standing for some time it is filtered, and the filtrate is tested for lead with chromate of potash. The black sulphuret of mercury left undissolved by the solution of the soda-salt, is washed with distilled water, dried, and mixed with dry carbonate of soda, in order to

be tested for mercury by ignition in a closed glass tube. If there be reason to suppose that tin may be present, as its separation from the above-mentioned metals is often effected imperfectly by sulphuret of ammonium, the apex of the tube is cut off after the ignition, the fused residue is dissolved in water, and further tested for tin.—*Jahresber. des Phys. Vereins zu Frankfurt am Main; Journal für Prakt. Chemie*, lxxiv. p. 350.

On the Behaviour of Basic Nitrate of Bismuth to an Aqueous Solution of Nitrate of Ammonia, and on the Separation of Bismuth from some Metals. By JULIUS LÖWE.

The author has found that basic nitrate of bismuth is not decomposed by washing, when this operation is performed with a very dilute cold solution of nitrate of ammonia. One part of this salt is dissolved in 500 parts of water.

Crystallized neutral nitrate of bismuth of the composition $BiO^3\,3NO^5+9HO$, is decomposed in a porcelain capsule with the quantity of warm water prescribed in the Prussian Pharmacopœia, the acid fluid covering the basic salt is evaporated to dryness in the water-bath in presence of the white precipitate formed, the residue is treated with a large quantity of water, and evaporated at the same temperature, and when this operation is repeated two or three times until the dry white residue in the water-bath does not betray the least trace of free nitric acid to the smell, a light saline mass of a beautiful white colour and of distinctly crystalline texture is obtained, exactly similar to the basic nitrate of bismuth precipitated by hot water.

It is not absolutely necessary for the preparation of this salt, that the quantity of hot water prescribed in the Pharmacopœia should be employed in the original precipitation, as this may be effected with smaller quantities. Care must be taken, however, that fresh water be added and again evaporated, until the neutral salt is completely decomposed, and all free nitric acid is driven off. It is easy to know whether fresh water is to be poured on, as the dull milk-white colour which the residue acquires in contact with fresh water may serve as an indication of incomplete decomposition, where a further addition of water is necessary. This method of preparing *Bismuthum nitricum præcipitatum*, which, according to the author's experiments, furnishes a faultless preparation, has also the advantage that the whole of the metal dissolved by the nitric acid is obtained in the form of basic salt, whilst hitherto the acid salt of the solution was lost.

In the analysis of a preparation thus obtained, the author found 80·471 per cent. of oxide of bismuth, agreeing with the formula ascribed by Jansen to the salt with 3 equivs. of water of crystallization $=2(5BiO^3,3NO^5+6HO)+(BiO^3,3NO^5)$; this contains 80·430 per cent. of oxide of bismuth.

This process for the complete conversion of nitrate of bismuth into the basic salt may be employed for the quantitative determination of bismuth.

The nitric solution of bismuth is evaporated on the water-bath in a porcelain capsule until the neutral salt remains of the consistence of a syrup. This is then treated with hot distilled water and evaporated on the water-bath, and this process is repeated three or four times. The residuary dry, white, crystalline, saline mass is kept upon the hot water-bath until no odour of volatilized nitric acid is perceptible. The contents of the capsule are then allowed to cool completely, and afterwards treated with a cold solution of nitrate of ammonia (1 part of salt in 500 parts of water), with which they are left in contact for a short time, then filtered, and washed with solution of nitrate of ammonia. Sulphuret of ammonium and sulphuretted hydrogen give no indications of bismuth in the filtrate. The author made several determinations in this way, which turned out to be accurate.

To determine the bismuth in a sulphuret of bismuth, the latter must be oxidized by nitric acid, and the sulphuric acid precipitated with nitrate of baryta, when the remainder of the process is as above described.

Quantitative Separation of Oxide of Bismuth from Oxide of Lead.—The solution of the two oxides in nitric acid is evaporated to dryness in a porcelain capsule on the water-bath; the dry residue is taken up by distilled water, again evaporated and so forth, as above. When all free nitric acid is expelled, and the residue of bismuth is completely converted into basic salt, the capsule is allowed to cool with its contents, which are then treated with a cold aqueous solution of nitrate of ammonia of known strength. The solution is left for some time in contact with the solid residue, in order that the soluble nitrate of lead may be completely taken up by it. The solution of nitrate of lead is filtered off, and the insoluble basic nitrate of bismuth which remains is washed with the solution of nitrate of ammonia. The oxide of lead may be precipitated as sulphate. The washing must not be continued too long.

Quantitative Separation of Oxide of Bismuth from the Oxides of Copper, Lead, and Cadmium.—The solution of the oxides in nitric acid is treated as above by evaporation in the water-bath. When the decomposition with water has been repeated sufficiently often for the oxide of bismuth, the dry residue is left standing upon the hot water-bath until the neutral nitrate of copper, the decomposition of which commences at 149° F., is completely converted into bluish-green basic salt, when, on the addition of distilled water, no blue solution of neutral nitrate of copper is produced. As soon as the decomposition is completed, the residue is allowed to cool in the capsule, then treated with an aqueous solution of nitrate of ammonia, and washed with the same solution. The oxide of lead is determined in the filtrate by sulphuric acid, and after evaporation, &c., the oxide of cadmium by carbonate of potash. The residue of basic nitrates of bismuth and copper are dissolved in dilute nitric acid, and the two oxides are separated by carbonate of ammonia or cyanide of potassium.—*Jahrb. des Phys. Vereins zu Frankf. am Main; Journ. für Prakt. Chemie,* lxxiv. p. 341.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On a New Base produced by the Decomposition of Aldehyde-Ammonia. *By* MM. HEINTZ *and* WISLICENUS.

THIS base has already been examined, although only in an impure state, by Von Babo; it is constituted in accordance with the formula of oxide of ammonium, in which, however, each of the four equivs. of hydrogen is replaced by the radical $C^4 H^3$. Aldehyde-ammonia, when not quite dry, soon acquires a yellow colour, especially under the influence of light and heat, and at the same time evolves water and much ammonia. The temperature of the water-bath is sufficient to decompose a large quantity of aldehyde-ammonia in a short time; the operation is best carried on in a flask with a long, perpendicular condensing tube. Through this the ammonia escapes, whilst the aqueous vapours and those of the aldehyde-ammonia condense on the walls and flow back into the flask. Finally, there remains a brown, bitter mass, which, whilst still hot, is of the consistence of a syrup, but when all its water is evaporated becomes hard, cracked and resinous. This is the new base in an impure state. To prepare it pure it is dissolved in sulphuric acid, and the sulphate is precipitated by alcohol. To free it from intermixed ammoniacal salt, it is dissolved in water, and the base is thrown down by caustic potash in the form of brown flakes, which are collected upon a filter. Carbonic acid is then passed through the alcoholic solution; this combines with the excess of potash, but not with the new base. After complete desiccation the latter is extracted by absolute alcohol, leaving a residue of sulphate and carbonate of potash. When the whole of this purifying process had been repeated three or four times, the authors obtained a substance the analyses of which gave uniform results leading to a formula.

The perfectly pure base, when obtained from the alcoholic solution by evaporation, forms a resinous, perfectly non-crystalline,

cracked, and brittle mass of a bitter taste. Its colour by transmitted light is reddish brown; in reflected light it appears darker, with a violet tinge. Its surfaces and fracture exhibit a strong lustre. When triturated in a mortar it forms a yellowish-brown powder. In water it dissolves with great difficulty, but more in cold than in hot water; the solution froths like thin soap and water. Æther does not dissolve any of it, but alcohol unites with it in any quantity. Its solutions have a weak, but distinct, alkaline reaction. It is separated with difficulty from the last traces of hygroscopic water; nevertheless, in drying, it must not be too strongly heated, as it fuses below 356° F., and at that temperature becomes decomposed, evolving volatile empyreumatic products, and leaving a shining black coal. Amongst the volatile products of dry distillation, an oil with strong basic reactions, soluble in water and alcohol, makes its appearance together with ammonia and water; it consists of at least two different bodies. The separation and further investigation of these two bodies could not be effected, as the authors had only small quantities at their command, and these soon disappeared in consequence of the extraordinary ease with which they were decomposed into ammonia and a blackish-brown, insoluble powder, especially in the presence of acids. When dried at 246° F., two determinations of carbon and hydrogen and two of nitrogen gave the formula $C^{16} H^{13} NO^2$, or, written as hydrated oxide of ammonium,

$$N(C^4 H^3)^4 O + HO.$$

For this body the authors propose the name of *hydrated oxide of tetrelallylammonium*, regarding the radical $C^4 H^3$ as an alcohol homologous with allylic alcohol, but not yet prepared, of the formula $C^4 H^3 O + HO$; this they call *elallylic alcohol*, as, from analogy with the preparation of the ordinary allylic alcohol from propylene, this must be obtainable from elayle.

Oxide of tetrelallylammonium combines with acids, except carbonic acid, to form salts, which are usually readily soluble in water, but insoluble in absolute alcohol.

Hydrated chloride of tetrelallylammonium, obtained by dissolving the base in muriatic acid and evaporating the excess of the latter, is an uncrystallizable, very hygroscopic shining mass of a deep brown colour, with a strong tinge of violet. From two determinations of its chlorine and one combustion analysis, it possesses the formula $N(C^4 H^3)^4 Cl + HO$. When this is brought in contact with perchloride of platinum in an aqueous solution, a yellowish-brown, non-crystalline precipitate is thrown down; this, when dried at 302° F., has the formula $N(C^4 H^3)^4 Cl + PtCl^2$, but when only dried at 248° F. still retains one equiv. of water. Perchloride of gold also produces an exactly similar precipitate in an aqueous solution of chloride of tetrelallylammonium. When this is boiled it disappears with reduction of gold, which is deposited in microscopic octahedra.

With sulphuric acid the authors prepared two salts, a neutral and an acid salt. The former is produced by mixing the alcoholic solu-

tion with a quantity of sulphuric acid, diluted with alcohol not quite sufficient for complete precipitation; when dry, it has the aspect of the chloride, but does not deliquesce on exposure to the air. It contains 1 equiv. of base to 1 equiv. of acid, and when dried at 212°—248° F., it retains no water. If the sulphuric acid be added in excess, the acid salt is precipitated. This dissolves readily in water like the neutral salt, but is insoluble in alcohol and æther; it has a strong lustre and a foxy-red colour. Its formula is $2\,[N\,(C^4\,H^3)^4\,O] + HO + 3\,SO^3$.

The neutral oxalate is precipitated by mixing alcoholic solutions of oxalic acid and the base, when the latter remains in excess. It has the aspect of the neutral sulphate, and contains equal equivalents of base and acid. An acid salt, which is readily soluble in alcohol and rapidly attracts moisture from the atmosphere, is obtained when oxalic acid is added in excess. Tartaric acid also gives a compound insoluble in alcohol, and tannic acid one which is even insoluble in water.

This investigation is intimately related to one previously published by Natanson upon a hydrated oxide of ammonium in which only one equiv. of hydrogen is replaced by the radical $C^4\,H^3$. This "oxide of acetylammonium" of Natanson is very similar in its physical and chemical properties to the oxide of tetrelallylammonium of the authors. Its preparation from protochloride of elayle gives a decided support to the view according to which it is to be called oxide of elallylammonium.—*Bericht der Akad. der Wiss. zu Berlin*, 1858, p. 520.

On Toluylphenyle and Cumylphenyle. *By* Dr. C. Kraut.

It has been shown by the investigations of Gerhardt and List, that benzosalycilic acid is converted into benzoylphenyle with evolution of carbonic acid under the influence of heat. The author has obtained toluylphenyle and cumylphenyle by the same reaction.

Toluylphenyle, $C^{12}\,H^5\,O + C^{16}\,H^7\,O^3$.—For the preparation of this compound dry salycilate of soda is treated with an equivalent quantity of protochloride of toluyle, when a slight elevation of temperature occurs; it is then heated over the open fire until the odour of the chloride has disappeared. The chloride of sodium is extracted with difficulty by cold water from the mass produced, which, when cold, is solid and hard. It is therefore advisable to pour over it a mixture of water and æther or sulphuret of carbon, to shake it until complete solution has taken place, and then to remove the aqueous stratum with the pipette, and wash the solution of toluylsalycilic acid in æther or sulphuret of carbon, several times with water. Finally, the æther or sulphuret of carbon is evaporated by a gentle heat, and any adherent water over sulphuric acid, when the toluylsalycilic acid is obtained in the form of a yellowish, tenacious, amorphous mass, resembling Venice turpentine. If this be heated in a retort, remains of sulphuret of carbon, water, and protochloride of toluyle are first of all evolved, with strong frothing; at a higher

temperature, the fluid then boils, and toluylphenyle passes over in the form of a colourless oil, which solidifies in the neck of the retort and in the receiver. It still usually retains some adherent phenylous and toluylic acids. To remove these, the distillate is boiled for a few moments with very dilute solution of potash, and allowed to cool, to see whether the toluylphenyle solidifies in a crystalline form. If this be the case, it is crystallized after washing and pressing from æther and alcohol; in the opposite case, the treatment with solution of potash must be repeated.

Toluylphenyle crystallizes from alcohol or æther and alcohol in nacreous, white laminæ, the crystalline form of which was not determinable. The hot saturated solution solidifies on cooling. In its behaviour it shows the greatest similarity to benzoylphenyle; its odour is slightly geranium-like, but is only perceptible distinctly when heat is applied. Its analysis gave the following numbers:—

C	78·83	..	28=168		79·24
H	5·54	5·69	12	12	5·66
O	..	..	4	32	15·10

Cumylphenyle is obtained by the distillation of cuminosalycilic acid. If cuminophenyle be triturated with several times its weight of nitrate of soda, and the mixture be put into sulphuric acid, and heated to boiling, abundant red vapours are evolved; and when the cold mixture is poured into a large quantity of water, a yellowish-brown precipitate is thrown down. This, when washed, dissolves readily in ammonia, and is again thrown down by acids. A portion of it was converted into the baryta-salt by solution in baryta-water, precipitation of the excess of baryta by carbonic acid, and boiling and evaporating the filtered solution. The baryta-salt separated at first in films, but became crystalline by standing under the mother-liquor. It is yellow, and acquires a darker, reddish colour by exposure to the air. After drying over sulphuric acid, it lost nothing in weight at 248° F., and contained 20·48 per cent. of barium.

Dinitrocuminate of baryta contains 21·30 per cent. of barium. Another portion of the acid was converted into lime-salt, when a deep wine-red solution and yellowish-red acicular crystals were obtained. The salt dissolved readily in boiling water, and lost nothing in weight at 248° F.; after drying over sulphuric acid, it contained 8·03 per cent. of calcium.

Dinitrocuminate of lime contains 7·33 per cent. and the nitrocuminate 8·77 per cent. of calcium. The salt investigated was therefore either dinitrocuminate of lime, or a mixture of this with the nitrocuminate. At any rate, the cumylphenyle had been decomposed into its constituents by the treatment with nitrate of soda and sulphuric acid, and had formed no nitrocumylphenyle, as is the case when benzoylphenyle is treated with a mixture of nitric and sulphuric acids in an analogous manner.

It is remarkable that the fusing-points of the three homologous compounds, benzoyl-, toluyl-, and cumyl-phenyle, do not form either

a descending or ascending series. In repeated experiments the author found that the melting-point of

Benzoylphenyle was 151°—158° F., of
Toluylphenyle „ 160°—162° F., and of
Cumylphenyle „ 144°·6—146°·4 F.

The portions used were well crystallized, and exhibited all the characters of purity.—*Archiv der Pharmacie*, cxlviii. p. 271.

On the Reduction of Nitrobenzine by Sodium-alcohol.
By MM. Béchamp *and* Saint-Pierre.

In many cases alcohol behaves as a powerful reducing agent; the authors have tried its action upon the hyponitric derivatives of several hydrocarbons and organic acids with the view of comparing it with that of agents which so readily reduce nitrobenzine, nitronaphthaline, nitrobenzoic acid, &c., to the state of amide derivatives. They first investigated the action of alcohol and wood-spirit upon nitrobenzine in sealed tubes. The reaction only commences at 302° or 356° F.; the mixture becomes brown; and when the tubes are opened gases are evolved, these contain carbonic acid; but the authors have not yet ascertained the existence of any other known compound.

They then substituted sodium-alcohol for alcohol, when the nitrobenzine furnished the same products which are generated by it under the influence of an alcoholic solution of potash:—nitroxybenzide, nitrobenzide, aniline, oxalic acid, carbonic acid, and brown compounds. The equation of this curious reaction can apparently only be deduced by taking as the terms of the first member only nitrobenzine and potash. In fact, potash alone has no action; on the other hand, nitroxybenzide, nitrobenzide, and aniline, when compared with nitrobenzine, are products of reduction; they suppose the intervention of a reducing agent, for they contain all the carbon of the phene, and potash is rather an agent of oxidation. Oxalic acid, also, a necessary and constant product of the reaction, cannot originate from the phenic carbon; its origin here can only be in the alcohol. The latter therefore must apparently be introduced into the equation, and the authors have endeavoured to verify this opinion.

Aniline had hitherto only been sought for in the ultimate products of the dry distillation of nitrobenzine with an alcoholic solution of potash. The authors think that aniline must be formed simultaneously with the other products. They brought in contact 108 grms. of nitrobenzine and a butyraceous mass of alcohol and sodium-alcohol containing 44 grms. of the latter compound. At a temperature of about 149° F. the reaction becomes very brisk; alcohol distils over, and when the action has become quieter, the mass is heated to 194° F. to drive off the last portions. The solid residue was treated with æther, which dissolves a portion, in which the authors detected aniline. . . . . .

Aniline was formed first by the action of sodium-alcohol alone; then by the action of heat upon products no doubt containing nitroxybenzide, which splits into aniline, nitrobenzide, and a black compound which remains in the retort.

The portion not dissolved by æther is very soluble in water. When saturated with acetic acid, carbonic acid is evolved, and a brown precipitate is produced. The filtered liquid, treated with acetate of lead, threw down a white powder, which, when decomposed by sulphuretted hydrogen, furnished crystallized oxalic acid.

Sodium-alcohol therefore behaves in this case like a solution of soda in alcohol. The principal elements of the reaction are represented by the following equations:—

I. $2C^{12}H^5NO^4 + C^4H^6O^2 = H^{12}H^7N + C^{12}H^5N + C^4H^2O^8 + 2HO.$

Nitrobenzine. Alcohol. Aniline. Nitrobenzide. Oxalic acid.

II. $4C^{12}H^5NO^4 + C^4H^6O^2 = 4C^{12}H^5NO + 6HO + 4CO^2.$

Nitroxybenzide.

The following equation expresses the subsequent action of alcohol upon nitroxybenzide:—

III. $8C^{12}H^5NO + C^4H^6O^2 = 2C^{12}H^7N + 6C^{12}H^5N + 4CO^2 + 2HO.$

In order that these equations may be admitted, it must be proved that alcohol really takes part in the reaction. With this purpose the authors have made two experiments, one of which they describe as follows:—In an apparatus furnished with a suitable condenser, they brought in contact 2 equivs. of nitrobenzine and 1 equiv. of sodium-alcohol.

Weight of alcohol and of sodium-alcohol produced by 3·37 grms. of sodium	34·495
Nitrobenzine	35·000
Total weight of alcohol, sodium-alcohol, and nitrobenzine	69·495
Weight of residue after driving off the alcohol and water	43·368
Difference, alcohol and water evolved	26·127
Weight of alcohol and water collected	25·957
Loss	0·170

In this experiment, for 3·37 grms. of sodium, 9·96 grms. of sodium-alcohol are obtained; according to equation I., 35 grms. of nitrobenzine reacting correspond with 2·565 grms. of water, which should be driven off with the alcohol; now we have,—

Sodium-alcohol and alcohol	34·495	
——— alone	9·960	
Free alcohol	24·535	24·535
Water evolved		2·565
Sum of alcohol and water evolved		27·100
Loss of weight of balloon		26·127
Loss		0·973

The first equation is therefore verified as far as it can be, and the loss may be attributed to water still retained in the balloon, and to alcohol absorbed by the corks. The alcohol evolved had a boiling-point of 176° F., that employed in the experiment was absolute alcohol boiling at 174°·1 F. This alcohol was not rendered turbid by water, and after ebullition its odour was fresh, but it contained traces of ammonia, indicating a reaction in an abnormal direction, but too small to introduce any error into the principal result of the investigation.

The residue of this last operation had the same composition as in the first experiment. The ætherial solution contained aniline, a little nitroxybenzide which was isolated in a crystallized state, and products which, when distilled, furnished more aniline and nitrobenzide. The portion of the product of the reaction which dissolved in water, furnished a brown precipitate with acetic acid, as already stated. This compound was washed with water and æther, and finally, with dilute acetic acid to remove all trace of alkali; it is a brown powder, not crystallized, tasteless, and not volatile. When heated in a tube, it is decomposed suddenly with a sort of deflagration, producing a thick yellow vapour, a large amount of aniline, and a new black compound which appears to contain nitrogen. This latter body appears to be analogous, if not identical, with the black residue obtained by the distillation of nitroxybenzide.

The analysis of the brown precipitate gave—

Carbon	61·63 to 62·67
Hydrogen	4·86 to 5·54
Nitrogen	14·26

Comptes Rendus, Dec. 6, 1858, p. 924.

On Sulphobenzamic Acid. *By* A. Engelhardt.

Some time since Buckton and Hofmann showed that in the action of fuming sulphuric acid on nitryles, the latter are decomposed into ammonia and an acid group, which either combines directly with sulphuric acid to form a conjugate acid, or carbonic acid is evolved at the same time, and the residuum of the organic acid group then conjugates with the sulphuric acid.

Thus benzonitryle, when heated with strong sulphuric acid, furnishes a non-crystalline, semitransparent mass with a glassy fracture, which, when treated with carbonate of baryta, evolves ammonia, and produces the baryta-salts of sulphobenzoic and disulphobenzolic acids. This reaction may be expressed by the following equations:—

$$C^{14}H^5N + 2HO + 2H^2S^2O^3 = C^{14}H^5S^2O^{10} + \left.\begin{matrix}H\\NH^4\end{matrix}\right\} S^2O^8.$$

Sulphobenzoic acid.

$$C^{14}H^5N + 3H^2S^2O^8 = C^{12}H^6S^4O^{12} + \left.\begin{matrix}H\\NH^4\end{matrix}\right\} S^2O^8 + C^2O^4.$$

Disulphobenzolic acid.

In this reaction the elements of water no doubt take part, to which must be attributed the decomposition of the nitryle into ammonia and the acid group. For this reason the author thought that the reaction must be quite different when nitryle is treated with anhydrous sulphuric acid, and that when benzonitryle, for example, is treated with anhydrous sulphuric acid, amide compounds of sulphobenzoic acid must be obtained. When the author exposed benzonitryle to vapours of anhydrous sulphuric acid, he obtained, amongst other things, an acid of the composition $C^{14}H^7NS^2O^8$. To this the author gives the name of sulphobenzamic acid, because it has the same composition that the amide acids of the bibasic acids must possess.

$$\text{Sulphobenzoic acid } C^{14}H^4S^2\left.\begin{matrix}O^6\\H^2\end{matrix}\right\}O^4 = C^{14}H^6S^2O^{10},$$

$$\text{the amide acid of which is } NH^2\left(C^{14}H^4S^2\left.\begin{matrix}O^6\\H\end{matrix}\right)\right\}O^2 = C^{14}H^7NS^2O^8.$$

Besides this acid other products are obtained by the action of anhydrous sulphuric acid upon benzonitryle. When anhydrous sulphuric acid is distilled over from Nordhausen sulphuric acid into a receiver containing benzonitryle, the walls of the receiver, from the commencement of the action of the acid vapours, are covered with a crystalline body, and subsequently, when the distillation is stronger, every drop of sulphuric acid falling into the receiver combines with the benzonitryle with evolution of heat, and forms a crystalline body. It is necessary in this operation that the receiver should be strongly refrigerated, and the distillation of the sulphuric acid carried on as slowly as possible, because otherwise, instead of the crystalline body, an amorphous, glassy mass is obtained in the receiver, and this, when further elaborated, furnishes quite different products. Sulphuric acid was distilled over into the receiver until all the benzonitryle was converted into a crystalline mass.

The crystalline mass obtained in the receiver was exposed to the air for some time, and then treated with cold water in order to remove the sulphuric acid which might have been added in excess to the benzonitryle. The crystalline body remaining was dissolved in boiling alcohol. On the cooling of the alcoholic solution, acicular crystals sometimes separate*, after the removal of which from the alcoholic solution, when the latter has been a little diluted with æther, transparent rhombohedric crystals of the new sulphobenzamic acid are deposited on standing. The mother-liquor from which these rhombohedric crystals are deposited, separates oleaginous drops when diluted with water; these agree exactly in odour with benzoic æther; a crystalline product still remains in the solution.

In a second operation the crystalline product which was obtained by the direct action of anhydrous sulphuric acid upon benzonitryle,

* Similar acicular crystals are deposited from the aqueous solution with which the crude product originally obtained by the action of anhydrous sulphuric acid upon benzonitryle was treated.

was first treated with cold æther in order to remove any benzonitryle which might possibly have remained undecomposed; the crystalline mass remaining was then dissolved in boiling alcohol of spec. grav. 0·889. The alcoholic solution while still hot was mixed with a little water, when acicular crystals were deposited as in the former case. But from the mother-liquor of these crystals, after it had been diluted with an excess of water, the oleaginous drops of benzoic æther were deposited, and after these had been removed from the solution, spontaneous evaporation in the air furnished a crystalline mass, which was permeated by a thickly fluid, syrupous solution. This crystalline mass was first washed with water to remove the mother-liquor, then dissolved in alcohol and mixed with æther, when rhombohedric crystals of the acid were deposited in course of time. Both the mother-liquor and the water with which the crystalline mass had been washed, furnished, by spontaneous evaporation, crystals of sulphate of ammonia, and the syrupous fluid, from which ammonia was evolved by boiling with carbonate of baryta, furnished sulphate of baryta and a small quantity of a baryta-salt which was very readily soluble in water.

However the elaboration of the product obtained by the action of anhydrous sulphuric acid upon benzonitryle might be carried on, the acid which the author describes, whenever it is obtained, is always to be distinguished with extraordinary facility from other products obtained simultaneously with it, and indeed, independently of its acid reaction, by the form of the crystals both of the acid itself and of its baryta-salt.

The acid dissolves pretty easily in hot and sparingly in cold water; on the cooling of the aqueous solution it crystallizes readily in the form of rhombohedric crystals, but sometimes in that of needles, consisting of an aggregation of small rhombohedra. It dissolves with ease in boiling alcohol, and with more difficulty in cold. On the addition of æther to the hot alcoholic solution of the acid, the latter separates in course of time in the form of transparent rhombohedra. Sometimes the acid separates immediately in needles on the addition of æther, but these, when the fluid is agitated, become in time spontaneously converted into rhombohedra. The acid gives an intense red colour to blue litmus-paper, and dissolves carbonate of baryta and marble with evolution of carbonic acid. Zinc is not dissolved by it. When heated to 248° F., the crystals of the acid lose nothing in weight; when strongly ignited, they are decomposed, with evolution of benzonitryle, leaving a carbonaceous mass.

A hot aqueous solution of the acid was saturated with carbonate of baryta, the filtered solution evaporated to dryness, and the residue treated with boiling alcohol. The insoluble baryta-salt left by this treatment was recrystallized from a hot aqueous solution, when it was deposited in the form of beautiful prismatic crystals. This baryta-salt crystallizes with remarkable facility from a hot aqueous solution, and crystals of ½—1 centim. may easily be obtained from a very small quantity of the salt. The crystals are sometimes

opake, and are covered with striæ in the direction of the faces of the prism. The salt dissolves easily in hot, with difficulty in cold water; it contains water of crystallization, which is easily expelled at 176° F. When heated to redness in a covered crucible, the salt is decomposed, when, judging from the odour, benzonitryle is evolved and sulphate of baryta remains. The composition of the anhydrous salt is

$$C^{14}H^{6}BaNS^{2}O^{8},$$

and that of the hydrated salt,

$$C^{14}H^{6}BaNS^{2}O^{8}+4HO.$$

The analyses gave—

C	31·31	..	14=84	31·29
H	2·76	..	6 6	2·33
Ba	25·43	25·33	1 68·5	25·51
N	..	..	1 14	5·21
S	12·55	12·13	2 32	11·92
O	..	..	8 64	23·84

By drying the hydrated salt lost 11·65, 11·66, 11·93, 11·60 per cent. of water =4 equivs.; the formula $C^{14}H^{6}BaNS^{2}O^{8}+4HO$ requires 11·82 per cent.

The lime-salt, $C^{14}H^{6}CaNS^{2}O^{8}$, gave on analysis 9·02 per cent. of calcium. The formula requires 9·09 per cent.

By the action of anhydrous sulphuric acid upon benzonitryle, therefore, a compound of sulphuric acid with benzonitryle may be obtained without evolution of ammonia; but at the same time there is a decomposition into ammonia and the benzoic group. Other products are also obtained, the reaction being an extremely complicated one, because the reagents which were employed for the separation of the bodies in course of formation, act even upon the original product, as is proved by the above-mentioned formation of benzoic æther.—*Bull. de St. Pétersb.* xvi. p. 382.

On the Constitution of the Essential Oil of Rue.
By C. Greville Williams.

The essential oil procured by distillation of the rue plant with water, has already been examined by several chemists. It was analysed many years ago by Will*, who deduced from his analyses the expression $C^{28}H^{28}O^{3}$. But at that time far too little was known about the oxygenated essential oils to permit of their accurate investigation. A more minute series of experiments, made by Gerhardt in 1848†, led him to conclude that oil of rue consisted principally of the capric aldehyde, contaminated by a small quantity of some hydrocarbon. This view was considered to be confirmed by

* Ann. der. Chem. und Pharm. xxxv. 235.
† Ann. de Chim. et de Phys. [3] xxiv. 103.

the production of capric acid when the oil underwent oxidation by means of nitric acid. But the production of an acid containing C^{20} merely rendered it probable that the rue oil did not contain *less* than 20 equivalents of carbon; it was no proof that it did not contain *more*. In fact the action of nitric acid varies with its concentration.

Guided by ideas which need not now be detailed, I made in 1853 some experiments, with the intention of obtaining from oil of rue certain bodies of the capric series, but they only served to convince me that the views then entertained regarding the constitution of the oil were erroneous. Some curious reactions were observed, but the experiments diverging into other channels have not, as yet, been renewed. Previous to recommencing them, it has been thought necessary to make a fresh examination of the oil; the results form the subject of this communication.

On examination of Gerhardt's numbers, it will be found that, while two of his analyses agree exactly with the formula $C^{20}H^{20}O^2$, the vapour-density (5·83) exceeds the theoretical number (5·398) to a degree much greater than can be accounted for by an error of experiment; the number obtained being almost the correct value for the homologue C^2H^2 above the capric aldehyde. Moreover, the fluid analysed was purified by distillation only.

In this investigation use has been made of the invaluable reagent for the isolation and purification of aldehydes (and bodies of more or less analogous constitution), placed in the hands of chemists principally by the researches of M. Bertagnini. By its aid a perfect separation has been made of the aldehydes in oil of rue, enabling their nature to be clearly determined.

On submitting the crude oil to about a dozen fractional distillations, distillates were obtained from 160° to 238°. On treating them with the bisulphites of soda or ammonia, great differences became apparent in their behaviour. The portions boiling between 160° and 188° were scarcely affected; they floated above the solution of the bisulphite, and after contact for weeks, showed scarcely a trace of crystalline compound. The fluids boiling at intermediate points yielded more crystals as their point of ebullition became higher; and when a boiling-point of 210° was reached, the oil (treated as before) became semi-solid in about two hours; and from that temperature to 238°, the tendency to yield crystals on agitation with the bisulphites increased.

Bisulphite of ammonia was found to be a more convenient reagent than the corresponding salt of soda, the resulting salt being more crystalline, and procurable with greater ease in a state of purity. When the fractions distilling in the twelfth rectification at 232° and upwards were treated with bisulphite of ammonia, the whole solidified, in the course of twelve hours, to a crystalline mass of such firm texture, as to be with difficulty penetrated by a glass rod. The very last fractions distilling at 260° and upwards yielded less crystalline masses, retaining traces of an empyreumatic oil.

The analyses and vapour-density determinations described in this

paper were all made upon fluids obtained by the following process. The crystalline substance from the lower fractions was thrown upon a filter, and well washed with a saturated solution of bisulphite of ammonia, which mechanically carried away much of the oily impurities. The product of this operation was a snow-white mass with a rich pearly lustre. It was carefully removed to a fresh piece of filtering-paper, and, a few folds intervening, laid upon a porous tile. In the course of a few hours the mass became firm enough to be removed, and being folded in several fresh pieces of filtering-paper, was again placed between tiles and subjected to considerable pressure. This was repeated until the paper ceased to receive any stain. The crystalline solid was then transferred to a stoppered vessel, and gently heated with a strong solution of potash. In a short time the compound was decomposed, the aldehyde floating on the surface in the form of an oil.

The aldehyde thus procured was colourless; it possessed a pleasing fragrance, totally different from the nauseous odour of the plant itself. Its boiling-point, as first prepared, fluctuated considerably, arising partly from oxidation and consequent formation of other bodies, and partly from the presence of a small portion of another aldehyde. The oxidation could only be prevented by performing the operation in a current of hydrogen, an exceedingly inconvenient process in fractional distillations, the apparatus having to be taken apart every few minutes. In the course of the experiments a considerable number of specimens were obtained, but they all had the same composition and vapour-density. By carefully collecting the residues of the distillations, and redistilling in minute retorts, blown from glass tubing, about sixty grains of the second aldehyde were obtained, still however contaminated by some of the fluid having the lower formula.

The first aldehyde yielded on analysis the following numbers:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Carbon ...	77·65	77·47	77·54	77·92	77·75	77·85	77·77	77·76
Hydrogen	13·05	13·37	12·75	12·87	13·16	13·00	13·00	13·32
Oxygen ...	9·30	9·16	9·71	9·21	9·09	9·15	9·23	8·92

	Mean.		Calculation.	
Carbon.....	77·71	C^{22}	132	77·65
Hydrogen	13·07	H^{22}	22	12·94
Oxygen	9·22	O^{2}	16	9·41

The above combustions were made in the manner described in the first part of my paper "On some of the Products of the Destructive Distillation of Boghead Coal*."

The annexed values were obtained in two determinations of the density of the vapour. In order to prevent oxidation, the balloon was in each case filled with hydrogen previous to immersion in the bath.

* Chem. Gaz. vol. xvi. 1858.

	I.	II.
Temperature of the air	18°	16°
Temperature of the vapour....	247°	259°
Pressure	760	759·2 mm.
Excess of weight of balloon ..	·2220	·5770 grm.
Capacity of balloon.....	82·5	228·0 cub. cent.
Residual hydrogen	1·0	10·0 cub. cent.
Density of vapour	5·83	5·91

The formula $C^{22}H^{22}O^{2}$=4 volumes, requires—

22 volumes carbon vapour..	0·8290 . 22 =	18·2380
44 volumes hydrogen.....	0·0692 . 44 =	3·0448
2 volumes oxygen.....	1·1056 . 2 =	2·2112
		23·4940

$$\frac{23{\cdot}4940}{4} = 5{\cdot}8735$$

Experiment (mean).	Theory
5·87	5·874

The first of these experiments yielded the same number as that found by Gerhardt. It is somewhat remarkable that the vapour-density did not induce him to adopt a formula with 22 instead of 20 equivalents of carbon.

The specific gravity of the fluid was 0·8497 at 15°. During a cold night the aldehyde was converted into a solid crystalline mass, resembling camphor. Agitation will cause it to solidify when the temperature is as high as 7°.

Gerhardt made four analyses and one vapour-density determination of oil of rue, and it is worthy of notice that two of his analyses and the vapour-density agree better with the view now proposed of its constitution than with his own. His analyses were as follows:—

	a.	*b.*	*c.*	*d.*
Carbon	77·65	77·69	76·95	77.10
Hydrogen	12·80	12·87	12·85	12·95
Oxygen.....	9·55	10·44	10·20	9·95

The analysis *a* was made on the first portion of the distillate, *b* and *c* on the last third, and *d* by treating an alcoholic solution of oil of rue with gaseous hydrochloric acid, and reobtaining the aldehyde by the addition of water. It would appear that this last operation (supposed by him to yield an isomeric modification of the capric aldehyde) was in fact to some extent a process of purification, the liquid so prepared having a fruity odour, different from the oil merely purified by distillation, and therefore resembling the pure and fragrant aldehyde obtained by me.

Although the experiments detailed scarcely permit a doubt of the true nature of the substance (especially when the mode of purification is considered), still it was wished to place the matter beyond dispute. With this intention, the aldehyde obtained from the crystalline bisulphite was again treated with bisulphite of ammonia, and

the whole process of purification repeated. The annexed analysis was made upon the aldehyde so obtained.

	Experiment.	Calculation.
Carbon	77·67	77·65
Hydrogen	12·93	12·94
Oxygen	9·40	9·41

The existence of margaritic acid having been disproved, and it having been rendered certain that cocinic acid does not contain 22 equivalents of carbon, it follows that this is the first substance yet isolated belonging to the eleventh series of bodies homologous with the derivatives of the fatty acids. It is the hydruret of the negative radical euodyle homologous with acetyle. When carefully purified by distillation, it distils at 213° C.

The quantity in my possession was too small to permit of an examination of its derivatives. I had hoped to obtain euodic acid by the action of weak nitric acid upon the aldehyde, but the oxidation proceeds too far, the carbon being attacked with formation of capric acid. A barium salt gave on analysis 29·985 per cent. of barium; caprate of barium requires 28·642. During the action of the nitric acid, especially if it be not very weak, pelargonic acid is formed. A small quantity was also obtained of another substance, which was separated in the following manner. The acid solution, and the oily layer produced by cohobating euodic aldehyde and ordinary nitric acid diluted with its own bulk of water, were separated by means of a tap funnel. The oily liquid, on treatment with a strong solution of potash, partly dissolved, but, on filtration, a soft yellow substance remained on the paper. It dissolved in boiling alcohol, and separated on cooling in brilliant yellow spangles, exactly resembling chrysene as it appears when crystallized from Boghead naphtha. On examination it appeared to be the potassium salt of the highly singular substance described by Chiozza*, and which he regards as a compound of pelargonic acid with binoxide of nitrogen. He states that great difficulties were found in its analysis, owing to the strong tendency of the nitrogen, in the state in which it exists in the acid, to form nitrous or nitric acid, which, entering the potash apparatus, increases its weight, and in consequence causes the carbon to come out too high. The entire quantity at my disposal being only 0·2170 grm., a correct result on combustion was scarcely hoped for, especially as 0·02 had been used in a few almost microscopic preliminary experiments. The following result is, nevertheless, sufficient to identify the substance with that described by Chiozza.

		Calc. $C^{18}H^{17}KN^2O^8$.
Carbon	43·3	42·20
Hydrogen	7·2	6·64

By carefully treating the residues of the distillates, previously alluded to, a small quantity of the lauric aldehyde was obtained. It

* Compt. Rend. xxxv. 797 (1852).

was not quite free from euodic aldehyde. Its boiling-point is about 232° C. The following is the result of its analysis:—

	Experiment.		Calculation.	
Carbon	78·1	C^{24}	144	78·26
Hydrogen	12·9	H^{24}	24	13·04
Oxygen	9·0	O^{2}	16	8·70

The density of its vapour was found to be 6·182, a number considerably below that required by theory (6·366), but quite high enough, taken in conjunction with the analysis, to show the presence of lauric aldehyde in oil of rue.

The fluids accompanying the aldehydes in oil of rue were found not to be of much interest. That portion boiling at 154° was the most volatile. It evidently belongs to the already too numerous groups of bodies isomeric with oil of turpentine. It was not obtained quite free from an oxygenated oil. By repeated rectifications a portion was obtained yielding,—

	I.	II.
Carbon	84·63	84·88
Hydrogen	11·91	11·90
Oxygen	3·46	3·22

By cohobation over a fluid alloy of potassium and sodium, a portion of oxygen was removed without decomposition of the oil. Thus purified, a combustion gave—

Carbon.....	86·20
Hydrogen	12·16
Oxygen	1·64

But it was impossible to remove the whole of the oxygen in this manner; and although the object could have been attained by other methods, the trouble would have been out of proportion to the result.

Oil of rue contains, in addition to the aldehydes and terebinthinate oils, fluid hydrates of oil of turpentine. There even appeared to be fluids present homologous with borneol, but (although higher in the series) having a lower boiling-point than borneol itself, and probably, therefore, isomeric with the borneol series. The substance was obtained from the fluid refusing to combine with the alkaline bisulphites. One fluid boiling at 191° contained,—

		$C^{22}H^{20}O^{2}$ requires
Carbon	78·7	78·6
Hydrogen	11·7	11·9
Oxygen	9·6	9·5

Little attention was paid to these bodies, partly because they appeared to differ in different samples of oil, but chiefly because no positive guarantee of their purity could be obtained. The fact, however, was observed, that the above fluid, like borneol, yielded camphor when boiled with nitric acid.—*Philosophical Transactions*, 1858.

On Chlorous Acid. By Dr. J. Schiel.

Chlorous acid may be prepared with perfect ease and safety by the observance of a few precautions, but nothing further is given in this memoir upon the mode in which this preparation is to be carried on. Cold water absorbs 10—12 volumes of chlorous acid. The deep reddish-yellow solution may be kept for a long time without decomposition, and is of great value as an oxidizing, that is to say, disinfecting and bleaching fluid.

Several chlorites are capable of important technical application.

Chlorite of lead, under certain circumstances, forms with chloride of lead the compound $PbCl + 2(PbO, ClO^3)$.

Chlorite of lead explodes below the boiling heat of water, and not at 244° F. as stated by Millon.

With uric acid and urea chlorous acid furnishes remarkable substances.—Liebig's *Annalen*, cviii. p. 128.

Some Observations on the Amount of Picric Acid obtained from Botany Bay Resin. By Prof. Bolley.

The so-called *Yellow gum*, or Botany Bay resin (the resin of *Xanthorrhœa hastilis*), was indicated by Stenhouse, and subsequently by Warington and Böttger, as the most abundant source of picric acid. It was said to furnish 50 per cent. of picric acid, so that notwithstanding its high price, it was the most economical substance from which to obtain picric acid.

The author has had numerous experiments made on this subject by his pupils in the Pharmaceutical Laboratory at Zurich. In these the resin was treated with 10 times its weight of nitric acid in a retort, and the distillate repeatedly poured back. At the commencement strong effervescence and evolution of nitrous acid took place without any application of heat; the action was afterwards assisted by heat, and this was continued with return of the distillate until the mass in the retort was completely dissolved to a reddish-yellow fluid. This treatment furnished—

Experiment 1. 22·5 per cent. of picric acid (somewhat purified by combination with potash and reprecipitation by muriatic acid).

Experiment 2. 25·6 per cent. of picric acid (obtained by crystallization from the acid liquid).

Experiment 3. 15 per cent., and therewith a yellowish powder, consisting principally of woody fibre, partly converted into pyroxyline.

By treating the resin with alcohol until nothing more dissolved, there was found to be 16·68 per cent. of insoluble matter, of which 2·5 per cent. was ash. The portion insoluble in alcohol consisted principally of small fragments of wood. In experiments 1 and 2, but little was to be detected in the residue left undissolved by nitric acid. The difference in the results of these experiments and those made by others, may rather be attributed to impurities or differences in the composition of the raw material, than to differences in the mode

of preparation. The statement that 50 per cent. of picric acid may be obtained from the resin, can only be true in rare cases.—*Schweizerische Polytechn. Zeitschrift*, 1858, p. 125.

New Compound of Potassium, Iron, Copper, and Cyanogen. *By* Prof. Bolley

In a coppering fluid that had been kept for a long time, the author found brown, apparently regular octahedra, containing in 100 parts—

K	21·30		3	21·22
Cu	22·64		4	22·86
Fe	10·11		2	10·10
N	17·41	32·98 Cy	7	32·83
C	15·57			
HO	13·24		8	13·63

The formula of this compound is therefore $3KCy+2CuCy$, $2FeCy+8HO$. The same compound was obtained by Moldenhauer by boiling protocyanide of copper with ferrocyanide of potassium.—*Journ. für Prakt Chemie*, lxxiv. p. 256.

ANALYTICAL CHEMISTRY.

On the Estimation of Iodine in Kelp, and the Approximate Separation of Iodine and Chlorine. *By* W. Wallace, Ph.D., F.C.S., *and* John Lamont*.

The preparation of iodine and potash-salts from kelp forms one of the many important manufactures conducted in Glasgow. The average quantity of kelp annually brought to this city amounts to 5000 tons, and the price ranges from £2 10*s.* to £12 per ton. The value of the iodine obtained from the kelp varies from $\frac{1}{5}$ to $\frac{1}{2}$ of that of the whole products, hence the price of the kelp is regulated chiefly by the amount of iodine it is expected to yield. An accurate and simple method for the estimation of iodine in kelp is therefore a desideratum of considerable importance, but no process fulfilling at once both of these conditions has yet been published.

Dr. R. D. Thomson has given the most reliable process hitherto made known†. It is based upon Lassaigne's method of estimating iodine by protochloride of palladium.

Dr. Penny's method‡ depends upon the reaction that occurs between bichromate of potash and an iodide, in presence of hydrochloric acid. This process gives excellent results with iodide of potassium, but the presence of sulphur compounds in kelp renders it inapplicable to the estimation of iodine in that highly complex

* Communicated by the Authors.

† Trans. Phil. Soc. of Glasgow, iii. 216. ‡ Chem. Gaz. 1852, 309.

mixture. The author of the paper referred to says, "The direct application of the present process to kelp and kelp-liquors is evidently inadmissible, in consequence of the sulphides, sulphites, hyposulphites, and sulphocyanides which they invariably contain. All these ingredients act readily upon bichromate of potash, in presence of hydrochloric acid. They may, however, be effectually removed by cautiously treating the solution from the kelp with hydrochloric acid, and evaporating to dryness, repeating the operations if necessary, or till the above ingredients are decomposed." We have tried this process very carefully, but have not succeeded in completely decomposing the sulphites and hyposulphites, without at the same time expelling a portion of the iodine.

The separation or decomposition of the sulphur compounds is attended with some difficulty, since most of the agents which cause their decomposition, act also upon alkaline iodides. Schönbein* has shown that binoxide of manganese, sesquioxide of iron, and many other oxidizing substances, liberate iodine when heated with its compounds; and we have found that when iodide of potassium is heated with binoxide of manganese for a few minutes, the iodine is expelled so completely that not a trace of that element can be detected in the ignited residue. We consider that this method of separating iodine from its combinations might be applied on the large scale. We have used it in the estimation of iodine in kelp-liquor (the free iodine having been converted into iodide of zinc, and subsequently estimated as iodide of silver), but we prefer the process about to be described. Of all the oxidizing agents we have tried, nitrate of potash is the only one that has yielded satisfactory results.

The process now given is the result of a great number of experiments made with the object of finding out a simple and at the same time tolerably accurate method for the estimation of iodine in kelp. It has been found to furnish results somewhat higher than those obtained by practical working on the large scale, but this is to be expected, as a considerable proportion of the iodine is lost in the potash-salts.

500 grains of the pulverized and well-mixed sample of kelp are boiled with water, and the liquor and washings are nearly, but not quite, neutralized with nitric acid, and evaporated to a small bulk. The concentrated liquid is transferred to a platina capsule, and evaporated to dryness. The residue is then fused by the application of a stronger heat, and kept in this condition for a few minutes, when all the sulphur compounds are converted into sulphates, without danger of decomposing the iodide. The fused mass is dissolved in water, the solution filtered if necessary, and from 3 to 8 or 9 grains of nitrate of silver are added, according to the description of kelp under examination. The mixture is heated and vigorously shaken, when all the iodine is precipitated, together with a portion of the chlorine. Instead of employing a known weight of nitrate of silver, a solution of that salt may be added in small successive portions,

* Chem. Gaz. 1850, 166.

with brisk agitation, until the precipitate produced on a further addition is perfectly colourless. Nitric acid is now added in excess, and the mixture is well washed by decantation. The last washing is decanted as completely as possible, and 250 grain measures or half an ounce of the strongest liquid ammonia is added, and the mixture vigorously shaken. The whole process is conveniently conducted in a small flask which is tightly corked after the ammonia has been introduced. The digestion is continued for several hours, after which the iodide of silver is collected on a small tared filter and washed, first with liquid ammonia, and subsequently with hot water, and dried. The weight of the iodide of silver +·1 gr. (dissolved by the ammonia), divided by 5 and multiplied by ·54, gives the per-centage amount of iodine in the sample, and this multiplied by 25·2, gives the number of pounds of iodine per kelp ton (22½ cwt.).

Three experiments with West Highland cutweed kelp gave respectively ·162, ·175, and ·167 per cent.; mean of three trials ·168=4·23 lbs. iodine per ton.

For kelp-liquors a modified process must be adopted. A cubic inch of the liquor is *nearly* neutralized with sulphuric acid, and boiled down to a small bulk; water is added, and the solution is filtered to separate sulphur. The solution is now evaporated to dryness, the residue is fused by the application of a gentle heat, and nitrate of potash is introduced in small successive portions until the fused mass is quite white, showing that all the sulphur has been oxidized. The analysis is now proceeded with in the manner already described. Care must be taken to use a sufficient quantity of ammonia, as the precipitate is usually bulky, and in the case of "finished ley," half a cubic inch will be sufficient. The amount of iodine obtained is multiplied by 1728 to find the quantity in a cubic foot, or 277 to calculate to a gallon, these numbers being, of course, doubled when half a cubic inch is used.

To estimate the proportion of iodine in the various salts obtained from kelp, 1000 grs. are dried and heated with a little nitrate of potash to decompose the sulphur compound, the result dissolved in water, and a large proportion of the salts crystallized out. The mother-liquor is treated with nitrate of silver, as described under kelp. The following results were obtained from salts crystallized from Highland cutweed kelp:—

"Muriate of potash"	·72 lb. per ton.
"Granulated sulphate"	1·21 „ „ „
"Alkaline salt" (not washed)	3·45 lbs. „ „

The method of analysis described above is applicable generally to the approximate estimation of iodine in mixtures containing chlorine, especially in cases where the proportion of iodine is minute. It

is based upon two well-established and well-known facts*, viz. that when nitrate of silver is added to a solution containing iodine and chlorine, the iodine is thrown down first; and that iodide of silver is only sparingly soluble in liquid ammonia, while chloride of silver is freely soluble in that liquid.

The solubility of iodide and of chloride of silver was accurately determined. Recently precipitated and well-washed iodide of silver was digested in liquid ammonia (spec. grav. ·890) with frequent agitation for 24 hours. 315 grain measures gave ·13; 230 grain measures gave ·09; 250 grain measures gave ·10. Mean of three experiments:—1 part of iodide of silver is soluble in 2493 parts (measure) of liquid ammonia. 225 grain measures of a carefully prepared solution of chloride of silver in strong liquid ammonia gave 17·47 grs.; 1 part is therefore soluble in 12·88 parts (measure) of liquid ammonia.

The following results of a series of experiments show that chloride of silver is capable of being dissolved out by liquid ammonia very completely from a mixture of iodide and chloride. In each of the experiments the whole of the iodine and chlorine was precipitated by nitrate of silver; the precipitate was well washed and digested for a considerable time with liquid ammonia, in quantity much more than sufficient to dissolve out all the chloride. The precipitate was collected on a small tared filter, and washed with strong ammonia, and subsequently with water. In each case an addition was made to the weight of the iodide of silver amounting to ·1 gr. for every 250 grain measures of ammonia employed, exclusive of that used for washing upon the filter.

I.	1	gr.	KI	and	9	grs.	NaCl	gave	1·6	gr.	AgI=1·12	KI.
II.	2	„	„	„	8	„	„	„	3·1	„	„	2·18 „
III.	3	„	„	„	7	„	„	„	4·3	„	„	3·03 „
IV.	5	„	„	„	5	„	„	„	7·0	„	„	4·95 „
V.	8	„	„	„	2	„	„	„	11·1	„	„	7·83 „

In the following experiments the chlorine was precipitated to a small extent only, and the chloride was dissolved out by ammonia in the manner already described.

I.	2·5	grs.	KI	and	10	grs.	NaCl	gave	3·5	grs.	AgI=2·47	KI.
II.	1	„	„	„	40	„	„	„	1·3	„	„	·92 „
III.	1	„	„	„	40	„	„	„	1·4	„	„	·99 „
IV.	·5	„	„	„	20	„	„	„	·7	„	„	·49 „

In detecting and estimating iodine in waters and solutions containing much chlorine and only minute traces of iodine, we recommend that nitrate of silver be added in moderate quantity with prolonged digestion and vigorous agitation, and that the precipitate so obtained be reduced by zinc and dilute sulphuric acid, and the iodine again partially precipitated by nitrate of silver.

* Compare Pisani, Chem. Gaz. 1857, p. 119; and Field, *ib.* p. 318.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Sarcine. *By* A. STRECKER.

THE mother-liquor left in the preparation of creatine by Liebig's method, contains, as is well known, creatinine, inosic acid, and paralactic acid. Besides these bodies, Scherer subsequently found inosite and volatile fatty acids. It was to be expected that by the continuation of investigations other definite bodies would be obtained. The author studied the behaviour of metallic salts towards the mother-liquor of creatine, and found that the body previously denominated sarcine by him, may be thrown down from it by several metallic salts.

If the mother-liquor of creatine be diluted with water, mixed with a solution of acetate of copper and boiled, a precipitate is produced containing oxide of copper and sarcine. This precipitate, when suspended in water, may be decomposed by sulphuretted hydrogen. The filtered solution then furnishes sarcine on evaporation. If this be again dissolved in water, treated with oxide of lead, which is again removed by sulphuretted hydrogen, and then evaporated, the sarcine is obtained quite pure. From the lead precipitate, a further portion of sarcine may be obtained by decomposition with sulphuretted hydrogen; this is likewise white, or but little coloured, the sulphuret of lead fixing the colouring matter. As, however, the sulphuret of lead also retains a portion of sarcine, it is best to treat it finally with ammonia, by which means the sarcine is all recovered in solution, and in a solid form by evaporation.

Sarcine, $C^{10}H^4N^4O^2$, separates on the cooling of the aqueous solution according to circumstances, either in flakes, which under the microscope appear as an accumulation of crystals, or in solid crusts and exfoliating scales. It dissolves in 300 parts of cold and 78 parts of boiling water, and in 900 parts of boiling alcohol. It dissolves more readily in acids, especially dilute muriatic acid, and

concentrated nitric or sulphuric acid. Sarcine diffused in water dissolves on the addition of a few drops of ammonia, potash, or baryta-water. On the addition of a little muriatic acid, or even of an excess of acetic acid, it separates again from the solution. The solution of sarcine in potash may also be thrown down by the passage of a current of carbonic acid.

Sarcine may be heated to 302° F., and probably still higher, without any change; when strongly heated it evolves an odour of hydrocyanic acid without fusing, whilst a not very volatile sublimate, evidently cyanuric acid, is formed, and a carbonized residue is left.

Sulphate of Sarcine forms colourless acicular crystals, and is decomposed by water.

Nitrate of Sarcine forms crystals resembling acetate of soda in appearance.

Muriate of Sarcine crystallizes in colourless tabular crystals with a nacreous lustre.

The Platinum double salt is obtained by the addition of bichloride of platinum to the concentrated hot solution of muriate of sarcine. On cooling, it forms yellow crystals, which, when washed with æther and alcohol, gave the following numbers on analysis :—

C	17·7	10=	60	17·5
H	1·7	5	5	1·5
N	..	4	56	16·4
O	..	2	16	4·6
Cl	..	3	106·5	31·1
Pt	29·2	1	99	28·9

Aqueous solution of sarcine gives no precipitates with most of the metallic salts in the cold, but frequently does so when ammonia or potash are added at the same time, or the solution is merely heated to boiling. Chloride and sulphate of zinc give no precipitates with solution of sarcine, but if an excess of ammonia be added, white flakes of a compound of sarcine and oxide of zinc are separated, which are but sparingly soluble in the boiling fluid. A solution of chloride of cadmium behaves in the same way. Sulphate of copper also gives no precipitate; but on the addition of a little potash, a pale blue precipitate is thrown down and undergoes no change by boiling. When more potash is added, the precipitate becomes black when boiled, and the sarcine passes into the alkaline solution. When a solution of sarcine is boiled with an excess of acetate of copper, a green flocculent precipitate is obtained.

Neutral and basic acetates of lead do not precipitate sarcine; in the latter case, boiling produces a white flocculent precipitate. By heating a solution of sarcine with hydrated oxide of lead, a solution of sarcine and oxide of lead possessing an alkaline reaction is obtained, whilst a portion of the sarcine is retained undissolved by the excess of oxide of lead.

The behaviour of sarcine towards nitrate of silver is so peculiarly characteristic, that it might be regarded as a reagent for sarcine. An aqueous solution of sarcine gives with it a flocculent precipitate,

which does not disappear on the addition of nitric acid in the cold; for its complete solution much nitric acid must be added, and the whole heated to boiling. On its cooling, small colourless crystalline scales of nitrate of silver and sarcine separate; under the microscope these are found to be separate, unentangled, fine needles. This compound is insoluble in water. Solution of nitrate of silver mixed with ammonia furnishes a gelatinous colourless precipitate with solution of sarcine; this appears like hydrate of alumina on the filter, and when dried in the air becomes converted into a hard mass, whilst its volume is greatly diminished. This precipitate is insoluble by boiling in water or ammonia.

The nitrate of sarcine and silver, $C^{10}H^4N^4O^2+AgO,NO^5$, gave on analysis—

C	20·4	20·0	10=	60	19·6
H	1·4	1·4	4	4	1·3
N	..	..	5	70	22·9
O	..	..	8	64	20·9
Ag	35·4	35·4	1	108	35·2

The compound of sarcine and oxide of silver precipitated from the ammoniacal solution of nitrate of silver has the composition—

$$C^{10}H^4N^4O^2+2AgO, \text{ or } C^{10}H^2Ag^2N^4O^2+2HO;$$

the substance dried at 248° F. is

$$C^{10}H^2Ag^2N^4O^2+HO.$$

Analysis of the latter:—

C	17·5	10=	60	16·7
H	0·9	3	3	0·8
N	..	4	56	15·6
O	..	3	24	6·7
Ag	60·0	2	216	60·2

Sarcine and Baryta, $C^{10}H^4N^4O^2+2(BaO,HO)$, or $C^{10}H^2Ba^2N^4O^2+4HO$.—Sarcine is readily soluble in dilute baryta-water; on the addition of cold saturated baryta-water, colourless transparent crystals of this compound separate. The crystals dried over sulphuric acid contain 49·6 per cent. of baryta.

The author prepared sarcine from the flesh of the horse, ox, and hare; it exists in them in far smaller quantity than creatine. 1000 parts of beef furnished 0·222 part of sarcine.

The author compares the behaviour of sarcine with that of guanine, showing a great similarity between the two bodies. The author also refers to the resemblance between sarcine and hypoxanthine and xanthine; Scherer has already indicated the identity of sarcine with hypoxanthine.—Liebig's *Annalen*, cviii. p. 129.

On Samaderine.

The *Samadera indica*, Gärtn. (*Vitmannia elliptica*, Vahl), called *Gatip Pahit* by the Malays, is a tree occurring in Java in the Regency of Bautam, and belonging, according to Bartling, to the class

of the *Terebinthinæ*, and the order *Simarubeæ*. C. L. Blume, who is at present residing in Java, has given a fuller description of this tree.

The tree is especially characterized by its numerous fruits, which, enclosed in coriaceous shells, are of the form of almonds, and weigh about $1\frac{1}{2}$ grm. They are very rich in oil, and are distinguished, as is also the bark of the tree, by a very bitter taste. This bitter is perhaps the bitterest in the whole vegetable kingdom, and is exceeded by no other known bitter matter. To this circumstance we are indebted for the preliminary investigation, for which M. Rost von Tonningen of Buitenzorg in Java furnished the material; this, however, will be carried on on a larger scale as soon as a greater quantity of the bark and fruits are collected and preserved.

100 parts of the fruits and bark of *Samadera indica* contain:—

	The fruits.	The bark.
Portions soluble in æther (oil)	34·260 (fat)	1·409
„ „ „ alcohol (resin)	8·380	5·119
„ „ „ water (tannic acid, samaderine, extractive matter, &c.)	10·585	1·203
„ „ „ potash (pectic acid)	0·160	traces
Mineral portions	2·733	7·931
Cellulose	39·000	70·656
Water	4·577	11·832
Loss	0·305	0·850

The properties of these bodies were as follow:—

The oil of the fruits is colourless, possesses a peculiar odour, no known taste, and is lighter than water; it burns with a yellowish-white and afterwards red flame, and forms soaps with alkalies.

The resin of the fruits is a brown substance of a very bitter taste, which attracts moisture rapidly from the air, and then deliquesces. Water dissolves a little of it, and this solution furnishes a black precipitate with solution of perchloride of iron (tannate). When heated it melts, becomes inflated, and burns very readily, diffusing a resinous odour, and leaving behind a pale grey ash which is almost soluble in water. It consists for the most part of chlorides of lime and potash with traces of iron.

The portions soluble in water are of a pale brown colour, and when evaporated leave an extract, which deliquesces in the air. They are as bitter as the alcoholic extracts, and consist of a mixture of extractive matter, sugar, tannic acid, and samaderine.

The ash which they leave after combustion, effervesces strongly with acids, and consists principally of chlorides of lime and potash.

The fat of the bark is pale yellow, has a neutral reaction, and possesses an oily bitter taste (caused by the solution of some samaderine in æther not quite free from water); it is of a soft resinous consistency, and may be drawn out into threads. It is only partially saponifiable, and consists of a mixture of fat and a resinous body.

The resin of the bark agrees nearly with that of the fruits, but its

aqueous solution furnishes a far stronger precipitate with perchloride of iron than that obtained from the fruits.

The portions of the bark soluble in water had the same properties as those of the fruits.

The most important constituent of the bark and fruits of *Samadera indica* is undoubtedly the samaderine contained in them. It is obtained by evaporating the aqueous decoction of the bark and fruit to the consistence of an extract; this is treated repeatedly with small quantities of alcohol, by which means the greatest part of the samaderine is left behind. It may be obtained pure by solution in water and treatment with animal charcoal.

Samaderine is of a brilliant white colour, laminarly and somewhat plumosely crystalline. Its taste is more persistently and intensely bitter than that of any other body with which the author is acquainted. When heated, it melts and evolves fumes which, when inhaled, possess a bitter and acrid taste; when the heat is continued, it becomes carbonized and burnt away, without leaving any trace of ash.

It dissolves in water more easily than in alcohol, and its solutions are perfectly neutral. It does not exert the least reaction upon ferridcyanide of potassium, sulphate of copper, nitrate of silver, chloride of platinum, tincture of iodine, protosulphate of iron, perchloride of iron, and chromate of potash. Nitric and muriatic acids give it a yellow colour, whilst by the addition of concentrated sulphuric acid a beautiful reddish-violet colour is produced, which disappears in course of time, and leaves a mass of feathery, strongly iridescent crystals, which will be more closely investigated hereafter.

Samaderine may be placed in the series of indifferent, crystallizable organic bodies, to which salicine, phloridzine, &c. belong. As soon as it has been prepared in larger quantities, further investigations upon it shall be published; the question will then also be solved, whether samaderine, which gives so distinct a reaction with sulphuric acid, is converted thereby into another compound and grape-sugar, like salicine and phloridzine.—*Archiv der Pharmacie*, cxlvi. p. 265.

On Oxalan. *By* Justus von Liebig.

Rosing and Schischkoff have described under the name of oxalan, a body which they obtained by the addition of alloxan to a solution of cyanide of ammonium. The author remarks that he has long employed the following reaction for the purpose of detecting alloxan in animal fluids. If a fluid contains alloxan, it furnishes, when mixed first with hydrocyanic acid and then with ammonia, and left to stand some time, a white precipitate of fine needles. If there be very little alloxan in a fluid, stirring with a glass rod is necessary in order to cause the separation of the crystals. The author expressly observes that he does not put forward any claim to priority in the discovery of this compound, but wishes to urge the abovementioned chemists to continue their investigations upon this body,

because their analytical results do not exactly agree in the amount of nitrogen with those obtained in the author's laboratory. The latter analyses gave—

	Mayer.		Rood.	
C	26·32	27·13	27·29	
H	3·98	4·33	3·84	
N	..	32·56	32·43	32·38

The determinations of nitrogen were effected by Rood by combustion with soda-lime. Dr. Thiel determined the relative proportion of the nitrogen to the carbonic acid, by the so-called qualitative method, and found on an average 124·5 vols. of carbonic acid to 64·5 of nitrogen, or 2 vols. of carbonic acid to 1 vol. of nitrogen. —Liebig's *Annalen*, cviii. p. 126.

Preparation of Platinum-black. *By* C. Brunner.

We possess several methods for the preparation of platinum in that state which is usually termed *platinum-black* on account of its black colour. In most of the recent modes of preparation, organic substances, such as alcohol, sugar, &c., are employed as reducing agents, by which means there is always a doubt whether a certain quantity, perhaps very small, of organic substance may not adhere to the preparation.

Perfectly pure platinum-black may be very easily obtained in the following way, without the employment of any organic substance :—

Dry peroxalate of iron (prepared by precipitating sulphate of iron with oxalic acid and washing) is heated in a shallow capsule until it begins to smoulder, when the heat is continued with stirring until the salt is entirely converted into peroxide. The extremely fine powder thus prepared, is reduced at an incipient red heat by a current of dry hydrogen gas in a glass tube. After it has become quite cold in the current of gas, the preparation, which is sometimes pyrophorous, is poured into a capsule with water, and gently crushed in it with a pestle. Of this metallic iron stirred up with water, small portions are then poured into a dilute solution of perchloride of platinum containing a small excess of muriatic acid, until this, after violent shaking and standing for some time, appears to be entirely deprived of colour. The precipitate obtained is then separated from the fluid by decantation, and boiled repeatedly with concentrated nitric acid until the extract contains no noticeable amount of iron, when the adherent nitric acid is removed by a weak solution of potash.

The preparation thus obtained is an amorphous black powder, which acquires an iron-like lustre by trituration in an agate mortar. When heated in a platinum spoon, it suddenly becomes ignited at about 392° F., and becomes converted into the ordinary form resembling spongy platinum, its volume at the same time being doubled. When moistened with a drop of alcohol, it also became ignited in a second or two, and converted into the ordinary form.

There is no doubt that the preparation will possess all the other known properties of platinum-black. Should this substance ever

be required in large quantities, the simplicity of this mode of preparation will recommend its adoption.—Dingler's *Polytechn. Journal*, cl. p. 376.

On Dinitrocuminic Acid. *By* C. Kraut.

By treating fused cuminic acid with nitrosulphuric acid, Cahours obtained a compound which he called dinitrocuminic acid, but which, according to him, possesses none of the properties of an acid. It does not, according to him, dissolve either in the cold or when heated in ammonia or solution of potash or soda, undergoes no change by the action of these bases, and does not combine with them. The author prepared dinitrocuminic acid by the method described by Cahours, and obtained the same compound which he prepared from cumylphenyle*, but which, like the latter, behaved as a well-characterized acid.

Cuminic acid dissolves, even in the cold, in large quantity in nitrosulphuric acid. A portion of the solution, after standing for a short time, was poured into water; the precipitated acid was collected, washed, and converted into the lime-salt. This formed yellow needles united in stars, which became darker by exposure to the air. The salt contained 8·54 per cent. of calcium; nitrocuminate of lime contains 8·77 per cent. of calcium.

Hence it appears that nitrocuminic acid is formed by the brief action of nitrosulphuric acid.

The remainder of the solution of cuminic acid in nitrosulphuric acid was left to stand until the following day, when crystalline masses had separated from it. Without removing these, the whole was poured into water, and the brown pulverulent precipitate was collected, washed and treated with carbonate of soda, in which it formed a clear solution. It was again precipitated from this solution by muriatic acid and boiled with milk of lime, but even by this means no insoluble portion could be separated; with an excess of lime there only remained some resin, and when the washing was imperfectly performed, some dinitrocuminic acid of the same properties as the dissolved portion. The compound insoluble in alkalies and alkaline carbonates, described by Cahours as possessing the formula of dinitrocuminic acid, could not consequently have been formed.

By precipitating the lime-salt by muriatic acid, washing the precipitate, and repeatedly recrystallizing it from alcohol, the acid was obtained pure. On the spontaneous evaporation of the alcohol, it shoots into pale yellow, well-developed crystals, which were found by Dauber of Gandersheim to belong to the triclinohedric system.

Dinitrocuminic Acid, $C^{20}(NO^4)^2H^{10}O^4$, when burnt with chromate of lead, with oxide of copper and a copper spiral before it, gave the following numbers:—

C	47·14	47·17	47·62	20 =	120	47·24
H	4·59	4·52	4·25	10	10	3·93
N				2	28	11·02
O				12	96	37·81

* See Chem. Gaz. No. 395, April 1, 1859.

The Lime-salt gave 7·01 per cent. of calcium. The formula $C^{20}\,Ca\,H^{9}\,(NO^{4})^{2}\,O^{4}$ requires 7·33 per cent.

The Silver-salt was obtained from the lime-salt by precipitating its aqueous solution with nitrate of silver. After recrystallization from boiling water, it forms pale yellow needles, which, when dry, scarcely undergo any change by exposure to light. It lost 5·26 per cent. of water at 212° Fahr., and then contained 29·76 per cent. of silver. We get for

$C^{20}\,Ag\,H^{9}\,(NO^{4})^{2}\,O^{4}+2\,Aq$ = 4·74 per cent. of water of crystallization,
$C^{20}\,Ag\,H^{9}\,(NO^{4})^{2}\,O^{4}$ = 29·91 per cent. of silver.

The Æther of dinitrocuminic acid, $C^{20}\,H^{9}\,C^{4}\,H^{5}\,(NO^{4})^{2}\,O^{4}$, is produced by the repeated passage of muriatic acid gas into an alcoholic solution of dinitrocuminic acid, and is thrown down from the solution by water in the form of a pulverulent precipitate. When purified by treatment with carbonate of soda, washing with water, pressure, and recrystallization from alcohol, it forms nearly colourless aggregated crystals, which fuse at 180°·5 F. Analysis gave—

C	50·44	24 =	144	51·07
H	5·56	14	14	4·97
N	..	2	28	9·93
O	..	12	96	34·03

The Amide of dinitrocuminic acid is obtained from the æther by ammonia. It crystallizes readily, even when in very small quantity, in thick yellow prisms, which are soluble in alcohol.—*Archiv der Pharm.* cxlvi. p. 273.

On Stasfurtite. By Prof. Heintz.

The mineral containing boracic acid, which occurs in Stasfurt, has, according to the analysis of Karsten, exactly the composition of boracite, a statement which has been confirmed by Chandler. Some quantitative determinations also, especially of the amount of magnesia in this mineral, which have been made under the direction of the author, appeared to confirm this supposition. But Ludwig has very recently shown that air-dried stasfurtite (not washed with water) contains more chloride of magnesium than can be washed out of it by water. He concludes, therefore, that stasfurtite is a compound of borate of magnesia with variable quantities of chloride of magnesia and water. The numbers found by analysis led him to the formula $5\,(3MgO+4BO^{3})+3MgCl+8HO$. As chemical compounds cannot be constituted in variable proportions, Heintz has made new analyses of stasfurtite.

He convinced himself, in the first place, that although water extracts a considerable quantity of chloride of magnesium from the mineral, a still larger quantity remains in it, notwithstanding long-continued washing. Even by repeated boiling with water, the chlorine cannot be altogether removed. Stasfurtite, therefore, is evidently a crystalline mineral, containing boracic acid and chlorine, penetrated by a solution of chloride of magnesium. If the com-

position of the former is to be ascertained, the latter must be removed by washing with water. Analyses of the mineral, washed sometimes with cold, sometimes with hot water, furnished nearly the same numbers, namely (No. V. was washed with hot water):—

	I.	II.	III.	IV.	V.
Magnesia.....	..	30·70	..	30·44	29·70
Peroxide of iron ..	..	0·52	0·41	0·36	0·94
Chlorine	..	8·21	..	..	8·07
Boracic acid	..	..	..	..	..
Water	1·63	..	..	..	..

The samples II. IV. and V. were obtained from different specimens. In the fifth analysis, the peroxide of iron still contained a considerable proportion of magnesia. If we omit the determination of the peroxide of iron and magnesia in the fifth analysis, as not being quite accurate, calculate the mean of the numbers found, and assume that the chlorine exists in the mineral as chloride of magnesium, we obtain the following composition for stasfurtite:—

	Found.	Calculated.	
Chlorine.....	8·14	7·74	1 Cl
Magnesium.....	2·84	2·70	1 Mg
Magnesia	25·74	26·67	6 MgO
Peroxide of iron..	0·43		
Boracic acid	61·22	69·93	8 BO^3
Water.....	1·63	1·96	1 HO

The formula expressing the composition of stasfurtite is therefore $2(3MgO+4BO^3)+MgCl, HO$. From the difference in the composition of this mineral and boracite, therefore, it appears that we are justified in giving the former the distinct name of stasfurtite, as Gustav Rose has done, from its physical and chemical properties.

H. Rose adds to this report, that in the boracite of Lüneberg also, both when opake and perfectly transparent, chlorine is an essential constituent, so that it does not consist of borate of magnesia, but is a double compound of borate of magnesia and chloride of magnesium.—*Bericht der Akad. der Wiss. zu Berlin*, 1858, p. 673.

On the Action of Chlorine upon Æther. *By* A. Lieben.

In a recent paper I described a substance which is obtained by the action of hydrochloric acid upon aldehyde, and the composition of which is expressed by the formula

$$\left.\begin{matrix} C^4H^4Cl \\ C^4H^4Cl \end{matrix}\right\} O^2.$$

Taking into consideration the composition, and also the properties of this substance, to which I gave the name of *oxychloride of ethylidene*, it may be regarded as æther in which 2 equivs. of hydrogen are replaced by 2 of chlorine. No chlorinated æther of this composition having hitherto been produced by the direct action of chlorine upon æther, I made some experiments to ascertain whether monochlorinated æther could be produced by this mode of action, and whether it would prove identical with the oxychloride of ethylidene.

A current of dry chlorine was passed into well-cooled anhydrous æther, until the gas appeared to have no action on the liquid at a temperature of 68°—86° F. On submitting the liquid to distillation, by which it is only slightly decomposed, and collecting the portion passing over between 284°—297°, I succeeded in obtaining a product which furnished on analysis 33·58 per cent. of carbon, 5·86 hydrogen, and 49·36 of chlorine, numbers which lead to the formula

$$\left.\begin{matrix} C^4 H^4 Cl \\ C^4 H^4 Cl \end{matrix}\right\} O^2,$$

representing æther, in which 2 equivs. of hydrogen are replaced by 2 of chlorine, and which should be called *monochlorinated æther*, assuming $C^4 H^5 O$ as the formula for æther.

The partial decomposition which it experiences by heat prevented me from determining its vapour-density. It forms a colourless limpid liquid with an acrid odour, and burning with a luminous flame with a green margin. It is neutral to litmus paper, but the spot made on the blue paper very rapidly turns red in the air. Its density at 73° is 1·174. It is isomeric with d'Arcet's chloretheral and with the oxychloride of ethylidene. From the latter, which it otherwise closely resembles, it differs by its specific gravity, and especially by its higher boiling-point.

Monochlorinated æther appears to be the sole body produced by the action of chlorine upon pure æther under the circumstances above described, excepting, perhaps, a small quantity of Malaguti's chlorinated æther, $C^4 H^3 Cl^2 O$. What passes over before 284° is a mixture of monochlorinated æther and æther.

It was natural to suppose that the monochlorinated æther would be decomposed by water and furnish aldehyde, but the resulting substance, although it reduces oxide of silver, differs from aldehyde. However, from the decomposition not being complete, I was prevented from isolating the new product. To complete the action I had recourse to solution of potash, which has a violent action both on the æther itself and also on the product obtained by the action of water; the mass becomes black, deposits crystals of chloride of potassium, and a small quantity of resin. On distillation alcohol passes over, and the residue contains *acetic acid.*

From this it is evident that the action of water and that of potash upon the monochlorinated æther are not identical; the first gives rise to a substance which reduces oxide of silver, and is probably isomeric with aldehyde, while under the influence of potash this substance splits up into alcohol and acetic acid by a reaction analogous to that which takes place with the hydruret of benzoyle, which, on treatment with an alcoholic solution of potash, decomposes into toluenic alcohol and benzoic acid. These relations may be expressed by the following equations:—

$$C^8 H^8 Cl^2 O^2 + 2HO = C^8 H^8 O^4 + 2HCl,$$

$$\left.\begin{matrix} C^8 H^8 O^4 + \begin{matrix} K \\ H \end{matrix} \end{matrix}\right\} O^2 = \left.\begin{matrix} C^4 H^5 \\ H \end{matrix}\right\} O^2 + \left.\begin{matrix} C^4 H^3 O^2 \\ K \end{matrix}\right\} O^2.$$

Comptes Rendus, March 28, p. 647.

On the Conversion of Guanine into Xanthine. *By* A. Strecker.

The composition of sarcine stands in the same relation to that of guanine as that of benzoic acid to that of benzamic acid, or acetic acid to glycocoll, as is shown by the following equations:—

$$\underbrace{C^{10}H^5N^5O^2}_{\text{Guanine.}} = \underbrace{C^{10}H^4N^4O^2}_{\text{Sarcine.}} + NH.$$

$$\underbrace{C^{14}H^7NO^4}_{\text{Benzamic acid.}} = \underbrace{C^{14}H^6O^4}_{\text{Benzoic acid.}} + NH.$$

$$\underbrace{C^4H^5NO^4}_{\text{Glycocoll.}} = \underbrace{C^4H^4O^4}_{\text{Acetic acid.}} + NH$$

The author endeavoured to obtain sarcine from guanine, and found that guanine could be converted into xanthine.

If guanine be treated with nitric acid, a yellow body is produced. If this be dissolved in muriatic acid, it furnishes a yellow solution, which loses its colour on the addition of metallic zinc or iron and long exposure to heat; on the addition of an excess of potash (when zinc is employed as the reducing agent), a colourless solution is obtained, from which acetic acid separates an abundance of colourless flakes. If, on the contrary, iron be employed for the reduction, a precipitate of hydrated protoxide of iron is obtained on the addition of potash, and the filtrate behaves towards acetic acid in the same way as when zinc is employed.

The reduction takes place, however, far more readily in alkaline fluids; if the yellowish-red solution of the nitro-body in solution of potash be mixed with a solution of sulphate of iron and heated to boiling, black proto-peroxide of iron is obtained, and the alkaline solution filtered therefrom is completely deprived of colour; on the addition of acetic acid, it furnishes a flocculent colourless precipitate, which is collected upon a filter, and washed with cold water.

This body dissolves completely, although with difficulty, in boiling water; on complete cooling a portion of the dissolved matter gradually separates in colourless flakes. Sometimes, however, a deposit took place even with the slightest cooling of the solution which had been filtered whilst boiling; in this case the solution became milky, and a fine powder was obtained instead of a flocculent precipitate, whilst the fluid did not become perfectly clear even by standing for weeks. Under the microscope, neither the flocculent nor the pulverulent precipitate exhibit any crystalline structure. Both appear as roundish granules, which in the former seem to be arranged in a row, whilst in the latter they are separate. This body dissolves in 723 parts of boiling, and 1950 parts of cold water. The cold aqueous solution of the body leaves it, on evaporation, in the form of scales or of an exfoliating connected film.

This body, when dry, forms a white or yellowish powder, which acquires a waxy lustre by pressure with the nail; it appears to be

Marcet's xanthine. Its analysis also corresponds with the composition of the latter, $C^{10}H^4N^4O^4$, giving

C	39·5	39·8	39·5	10=60	39·5
H	3·1	3·1	3·0	4 4	2·6
N	37·4	36·3	..	4 56	36·8
O	..	..	..	4 32	21·1

The conversion of guanine into xanthine is explicable, if we take no notice of the yellow intermediate product, by the equation:—

$$\underbrace{C^{10}H^5N^5O^2}_{\text{Guanine.}}+O^3=\underbrace{C^{10}H^4N^4O^4}_{\text{Xanthine.}}+HO+N$$

This equation corresponds with those by which the conversion of the amides into the corresponding acids, or of hippuric acid into benzoglycolic acid by oxidizing influences, may be expressed.

Air-dried xanthine lost little in weight at 212° F., and underwent no further change up to 302° F. When heated in a tube it gives off white fumes without melting, cyanogen gas and hydrocyanic acid being perceptible, whilst a crystalline sublimate is deposited, which, when further heated, allows a readily volatile portion (carbonate of ammonia) to escape, while another portion is carbonized.

In its combining proportions xanthine resembles guanine and sarcine, but its basic properties are weaker.

Sulphate of Xanthine is obtained by dissolving still moist xanthine in not very concentrated sulphuric acid; the fluid becomes heated, but remains colourless, and on cooling the salt separates in crystalline scales. If the sulphuric acid be then absorbed by porous porcelain, there remain light, nacreous crystals, which undergo no change by exposure to the air; water extracts all the acid from them. The sulphate contains 30·6 per cent. of sulphuric acid; the formula $C^{10}H^4N^4O^4+2(SHO^4)+2HO$ requires 29·8 per cent. of sulphuric acid.

Nitrate of Xanthine.—Xanthine dissolves, without evolution of gas, in concentrated nitric acid. On evaporation the salt is obtained in hemispherical or wart-like crystals, which consist of fine crystals. The salt was always yellow.

Muriate of Xanthine, $C^{10}H^4N^4O^4+HCl$, forms aggregations of acute rhombic laminæ, often interpenetrated. It dissolves in about 153 parts of water.

The Double Platinum-salt, $C^{10}H^4N^4O^4, HCl+PtCl^2$?, was obtained by mixing the hot solution of muriate of xanthine with bichloride of platinum; after long standing, acicular crystals of the double salt separated. They left 17 per cent. of platinum. The above formula requires 27 per cent., and the author therefore thinks that free muriate may have been mixed with the double salt.

Xanthine dissolves in alkalies; it dissolves with ease in ammonia, and on evaporation the ammonia is entirely dissipated. It dissolves still more readily in solution of potash; acetic or carbonic acid separate the greater part of it again in flakes. By boiling with baryta-water but little xanthine is dissolved, and the filtered solution depo-

sits nothing on cooling. The xanthine in this case combines with baryta to form a compound which is difficult of solution; it contains 47·1 per cent. of baryta. The formula $C^{10}H^4N^4O^4 + 2(BaO, HO)$ requires 47·4 per cent. of baryta.

By precipitating a solution of xanthine in ammonia with nitrate of silver, a colourless gelatinous precipitate is obtained; after washing with water containing ammonia, and drying at 248° F., it was analysed and contained 56·0 per cent. of silver. The formula $C^{10}H^4N^4O^4 + 2AgO$ requires 56·2 per cent. of silver.

Essentially different from this compound is the precipitate produced by nitrate of silver with xanthine in acid solutions. If a solution of xanthine in dilute nitric acid be mixed with nitrate of silver, a flocculent precipitate is formed, which dissolves when boiled, and separates again on cooling, but slowly in proportion as there is more nitric acid present. In the presence of a comparatively large quantity of nitric acid a separation only takes place after several days have elapsed, and in this case distinct aggregations of fine needles, resembling Wavellite, are formed; when the acid is more dilute, a coherent, film-like precipitate is obtained, which under the microscope appears to be composed of entangled capillary crystals. This precipitate appears to be a compound of xanthine with nitrate of silver, like the compound of sarcine or guanine. It is decomposed by washing with water, and at last contains no nitric acid and variable quantities of silver.

Analyses of such preparations gave—

Carbon.....	21·8	27·8	27·3
Hydrogen....	1·5	2·0	2·1
Silver	39·8	26·7	28·3

The cold saturated solution of xanthine in water gives a white precipitate with solution of bichloride of mercury; it furnishes no precipitate with acetate of copper in the cold, but when boiled yellowish green flakes separate. A solution of xanthine in ammonia gives white precipitates with ammoniacal solutions of chloride of cadmium and chloride of zinc; these are soluble in much ammonia; acetate of lead furnishes white flakes, which, by standing, are often converted into shining crystalline scales.

The author compared this xanthine with a sample of xanthine obtained from the same urinary calculus, which was formerly investigated by Liebig and Wöhler, and convinced himself that the xanthine prepared by him from guanine is identical with the xanthic oxide of Marcet, Liebig, and Wöhler.

The author is also of opinion that the statement made by Lieberkühn and Strahl, that human urine contains normal xanthine, is correct. The silver compound, prepared formerly by himself from human urine, exactly resembles the silver compound of xanthine; and lastly, guano itself appears to contain xanthine; at least, in preparing guanine, the author obtained a body which behaves like xanthine.

The yellow body above mentioned as being produced by the

treatment of guanine with nitric acid, has, according to Neubauer and Kerner, the formula $C^{10}H^5N^7O^{12}$, and is nitrate of nitroguanine. The author prepared this body, and obtained it with the properties described by the above-mentioned chemists, but with a variable constitution. His analyses gave—

Carbon ..	35·7	37·9	36·4	35·7	36·3	36·3	
Hydrogen	2·8	3·0	2·7	2·8	2·9	3·1	
Nitrogen	..	..	..	..	..	..	40·0

It is impossible to calculate a simple formula from these numbers, and it finally appeared that the yellow body is a mixture of xanthine with a yellow nitro-compound which is exceedingly similar to xanthine.

Thus, if the solution of the mixture in hot nitric acid be precipitated with nitrate of silver, the compound of xanthine and oxide of silver is principally dissolved, when the concentration has reached the right point, whilst the greater part of the nitro-compound remains. Colourless crystalline globules and coloured flakes, which may be mechanically separated, are deposited from the filtrate. Large quantities could not indeed be prepared in a pure state, but the reactions of the colourless crystals showed that they were the compound of (nitrate of) silver with xanthine, which has already been described.

As the analyses of the mixture showed a smaller amount of carbon and hydrogen, but a larger amount of nitrogen than exists in xanthine, the yellow body appears to be a nitrated product of xanthine, although it still remains doubtful whether its formula is

$$C^{10}\left\{\begin{matrix}H^3\\NO^2\end{matrix}\right\}N^4O^4, \text{ or } C^{10}\left\{\begin{matrix}H^3\\NO^4\end{matrix}\right\}N^4O^4.$$

The action of reducing agents upon the yellow body produced from guanine might consist in reproducing xanthine from its nitro-compound, so that the whole mixture is obtained as xanthine.

The identity of the yellow products of decomposition obtained from guanine, xanthine, and sarcine, is supported by their similar behaviour towards solution of potash and ammonia.

A regards the body obtained from sarcine by the action of fuming nitric acid, the author has found that the yellowish-red solution of it in potash is decolorized by sulphate of iron, and also that acetic acid precipitates from the colourless solution a body agreeing with xanthine in its properties. The author consequently looks upon it as proved that sarcine may be converted into xanthine as well as guanine.—Liebig's *Annalen*, cviii. p. 141.

On the Colouring Matter of the Bark of the Root of Lithospermum arvense. *By* Dr. A. Ludwig *and* A. Kromayer.

The thin woody roots of *Lithospermum arvense*, collected in June, are covered with a very thin brownish-red bark; the wood is white. For the separation of the colouring matter, the bark was shaved off,

during which operation a narcotic, opium-like odour was distinctly perceptible. These fragments of bark were exhausted with alcohol of spec. grav. 0·863, which was slightly acidulated with acetic acid. After the alcohol was distilled off, and the residue freed from traces of alcohol by evaporation, a black resin separated from the aqueous fluid.

This resin dissolves almost entirely in æther. The solution has a greyish-blue colour; during evaporation it exhibited a transitory red colour, especially when it was exposed to a strong current of air.

Concentrated sulphuric acid also dissolves the black resin, and thereby acquires a fine red colour; the addition of water causes the separation of the resin with a green colour. Nitric acid rapidly destroys the colouring matter with formation of yellowish-brown products of decomposition.

For further purification the black resin was dissolved in anhydrous æther, the solution filtered and the filtrate evaporated. The remaining colouring matter exhibited the same properties as before.

The entire mass was then treated with a concentrated solution of carbonate of soda; only a small quantity was dissolved. The solution had a blue colour. An excess of dilute sulphuric acid gave the mixture a fine red colour, and small red flakes separated from it after it had stood for some time; these dissolved with a red colour both in æther and alcohol.

These experiments were undertaken with the view of ascertaining whether the red colouring matter of the *Lithospermum arvense*, a plant belonging to the family *Borragineæ*, was identical with the anchusine of Bolley and Wydler (Alkannine, Alkanet-red), which occurs in *Alkanna tinctoria*, also a Boraginaceous plant. The *Lithospermum*-red certainly showed much resemblance to the Alkanet-red, but also many differences. Both behave similarly towards water, alcohol, æther, and alkalies. But the red of *Lithospermum* is dissolved by æther with a blue colour, whereas the ætherial solution of Alkanet-red is of a deep dark-red colour.

The red of *Lithospermum* appears to have originated from an essential oil.—*Archiv der Pharm.* cxlvi. p. 278.

On Oxide of Æthylene. *By* A. Wurtz.

When glycol saturated with muriatic acid is heated in a closed vessel, the two bodies combine, and at the same time water is eliminated. The result of this action is a neutral body, containing chlorine, a sort of muriatic æther produced in accordance with the following reaction:—

$$\underbrace{C^4H^6O^4}_{\text{Glycol.}} + HCl = \underbrace{C^4H^5ClO^2}_{\text{Monohydrochloric glycol.}} + H^2O^2.$$

I call this compound *monohydrochloric glycol*, Dutch liquor representing dihydrochloric glycol. It is a colourless liquid, neutral

to the taste, soluble in water, boiling at 262° F., and furnishing the following results on analysis:—

	Found.	Calculated.	
C	29·66	4	29·82
H	6·56	5	6·21
Cl	..	1	44·09
O	..	2	19·88

leading to the formula

$$C^4H^5ClO^2 = \left.\begin{matrix} C^4H^4 \\ H \\ Cl \end{matrix}\right\} O^2$$

Monohydrochloric glycol is instantaneously decomposed by a solution of potash, with formation of chloride of potassium and evolution of an inflammable gas, or rather vapour, which burns in the manner of olefiant gas itself. This body is oxide of æthylene, or oxide of olefiant gas, of which Dutch liquor constitutes the chloride. Its formation in the reaction of potash upon monohydrochloric glycol is easily explained. By losing the elements of muriatic acid, this chlorinated compound becomes converted into oxide of æthylene—

$$C^4H^5ClO^2 = C^4H^4O^2 + HCl.$$

The compositon of oxide of æthylene is shown by the following analyses:—

	Found.		Calculated.	
	I.	II.		
C	54·39	54·75	4	54·54
H	9·29	9·00	4	9·09
O	..	..	2	36·37

leading to the formula $C^4H^4O^2$.

This formula has been verified by the determination of the density of its vapour, which was effected by Gay-Lussac's method. The following are the data of the experiment:—

Weight of the substance	0·165
Barometer.....	746 millims.
Difference of level of the mercury	135 millims.
Temperature of the bath.....	163° F.
Volume at 163° F.	141·5 cubic centims.

From this we deduce for the vapour-density sought the number 1·422. Theory indicates the number 1·52. Oxide of æthylene is consequently isomeric with aldehyde. It is distinguished from it by some of its properties, and resembles it in others. Under a pressure of 0·7465 metre it boils at 56°·3 F., aldehyde boils at 69°·8 F. Like aldehyde, oxide of æthylene dissolves in water in all proportions, and combines with bisulphite of soda to form deliquescent crystals, endowed at the same time with a fresh and sulphurous taste. When mixed with ammoniacal æther, it does not form the well-known crystals which characterize aldehyde. Perchloride of phosphorus attacks it with extreme violence, and converts it into chloride

of æthylene, at the same time oxychloride of phosphorus is formed—

$$PCl^5 + C^4H^4O^2 = PO^2Cl^3 + C^4H^4Cl^2.$$

Thus this compound presents some of the characters of the aldehydes, and inaugurates a new series of bodies, exhibiting the most curious relations of isomerism with the aldehydes properly so called.

By treating propyloglycol successively with muriatic acid gas and with potash, I obtained the second term of this new series, oxide of propylene, $C^6H^6.O^2$, which is isomeric with propionic aldehyde. If the aldehydes, properly so called, be the hydrurets of oxygenated radicals, the compounds now described are the oxides of diatomic hydrocarbons. These relations are explained by the formulæ:—

$$\underbrace{\left.\begin{matrix} C^4H^3O^2 \\ H \end{matrix}\right\}}_{\text{Aldehyde.}} \qquad \underbrace{C^4H^4.O^2}_{\text{Oxide of æthylene.}}$$

$$\underbrace{\left.\begin{matrix} C^6H^5O^2 \\ H \end{matrix}\right\}}_{\text{Propionic aldehyde.}} \qquad \underbrace{C^6H^6.O^2}_{\text{Oxide of propylene.}}$$

The oxides of æthylene and propylene represent, in my opinion, the true æthers of the glycols; for they are capable of regenerating the chlorides, and consequently the corresponding glycols. In truth, it is the ordinary alcohols that are produced when glycols are dehydrated by chloride of zinc; but it is in virtue of an energetic reaction, far less distinctly marked than the preceding, and capable of giving rise to a molecular transformation of the products formed otherwise at a high temperature. Moreover, as I have already pointed out in a former communication, the ordinary aldehydes are not capable of regenerating the combinations of the glycols from which they originated.

The author concludes with a summary of the general results of his investigation of the glycols, which has occupied him for three years, in the following words:—

"The existence of glycol does not constitute an isolated fact in science. On the one hand it has been generalized by the discovery of the superior glycols, on the other it serves for the explanation and connexion of a multitude of facts which were scattered without coordination.

"The glycols, now four in number, arranged in a series parallel to that of the true alcohols, closely allied by their composition and by their general chemical and physical properties, form, so to speak, the bridge between the alcohols and glycerine, just as their combinations mark the passage between the æthers and the fatty bodies;

"Glycolic, lactic, and oxalic acids formed by synthesis, and derived from the glycols as acetic acid is derived from alcohol, and in general the bibasic acids referred to bibasic or diatomic alcohols;

"The aldehydes obtained with the glycols by a simple dehydratation, and by the side of this series of aldehydes which have long been known a new series of bodies isomeric with the former, and constituting the true æthers of the glycols;

"Dutch liquor and its numerous analogues, related to the glycols of which they represent the muriatic æthers."

Such are the general consequences which follow immediately from the facts related in my memoir. They are of a nature to exercise a certain influence upon the reigning theories. This I shall now try to establish.

My experiments have shown that æthylene or olefiant gas is a diatomic radical. In fact, when chloride of æthylene is decomposed under the influence of salts of silver, the radical remains intact, and takes the place of 2 equivs. of silver. This is the theoretical interest of this investigation; it has been proved that an organic group combined with 2 equivs. of chlorine or bromine, may, on abandoning them, take the place of 2 equivs. of silver. This fact appears to me to be new and important. I have endeavoured to generalize it, not only by operating upon other bromides analogous to bromide of æthylene, but also by demonstrating that a radical, combined with 3 equivs. of bromine, may take the place of 3 equivs. of silver. The experiments made upon the transformation of iodide of allyle into glycerine have furnished me with the proof of this. In my opinion the striking part of these experiments is not the discovery of a new body, glycol; one does not care about new bodies in organic chemistry; it is not the fact itself, or the overcome difficulty of the artificial formation of glycerine, but it is the mode of formation of glycol; it is by foreseen reactions that we have been enabled to realize the formation of this body, itself foreseen; it is the transformations the group allyle of the iodide has been made to undergo in order to regenerate glycerine. All these experiments, directed towards the same end, prove that an organic group combined with 2 atoms of chlorine or bromine is equivalent to 2 atoms of hydrogen, and that an organic group combined with 3 atoms of chlorine or bromine is equivalent to 3 atoms of hydrogen. Thus the doctrine of polyatomic radicals obtains entrance into science supported by facts. It was before only a vague and unsupported hypothesis.—*Comptes Rendus*, January 10, 1859, p. 101.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Saponification of Fatty Bodies by means of Chloride of Zinc. *By* Léon Krafft *and* Tessié du Mottay.

The object of the authors' investigations was the discovery for some South American merchants of the means of transforming the fatty bodies of their countries into stearic acid, and afterwards into

candles. The conveyance of sulphuric acid by sea was to be avoided, on account of its danger.

Struck by the great analogy of the action of sulphuric acid and chloride of zinc upon organic matters, they thought of applying the latter to the saponification of the neutral fatty bodies. Economically the idea was very feasible, as fused chloride of zinc may be obtained at Marseilles for 25 francs per 100 kilogrammes; when packed in cases or casks, it may be conveyed anywhere without inconvenience. The application remained to be realized.

When any neutral fatty body is heated with anhydrous chloride of zinc, the latter melts and disappears as the temperature rises. Between 302° and 392° F. the mixture of the two bodies is complete. If the temperature be then sustained for some time, and the product washed several times with hot water, or, still better, with water acidulated by hydrochloric acid, a fatty body is obtained, which, when distilled, furnishes the corresponding fatty acids, with an insignificant production of acroleine The washing-waters carry off nearly all the chloride of zinc employed, which can be again prepared for use by evaporation. The fatty acids are thus produced in as great quantity as by the ordinary methods; they have the same aspect, qualities and melting-point as those produced in manufactories where the distillation is effected after the sulphuric saponification. To operate well and quickly, the mixture of the neutral fatty body and chloride of zinc must be heated rapidly until the moment when, in consequence of the violent reaction of the two bodies upon each other, aqueous vapours are evolved in abundance.

The washing with acidulated water after saponification may be avoided, but then the products of the distillation are softer. If the distillation be hastened by means of a current of superheated steam, this defect may be corrected in a great degree. In all cases steam allows harder and less coloured products to be obtained with rapidity. The quantity of chloride of zinc necessary for a good saponification varies from 8 to 12 per cent. of the weight of the neutral fatty body.

The following are some of the authors' experiments:—

Tallow.—*Experiment* 1. 300 parts of tallow, fusible at 100° F. After saponification and washing, 284; loss by saponification, 5 per cent. After distillation with steam, 250 parts of substance fusible at 113° F.; loss by distillation, 13 per cent.

Experiment 2. 2000 parts of fat fusible at 100° F., and 240 parts, or 12 per cent. of chloride of zinc. After saponification the fusing-point was 107°·6 F.; and after distillation, without steam, 113° F. Chloride of zinc recovered, 215 parts.

Palm-oil.—*Experiment* 1. 2160 parts of palm-butter fusible at 75° F., and 12 per cent., or 260 parts of chloride of zinc. The product of saponification was fusible at 95° F., and that of distillation (without steam) at 115° F. Chloride of zinc recovered, 211.

Experiment 2. Palm-butter. 195 of saponified product gave 175 of fatty body, fusible at 122° F.

Experiment 3. 300 of palm-oil; after saponification, 290; loss, 3·3 per cent. 260 parts fractionally distilled with steam gave—

First product....	155	white crystallized, fusible at 131° F.
Second product..	32	yellowish „ „ „ 91°·4 F.
Third product ..	55	greenish yellow, consistence of honey.
	242	

Cocoa-nut Oil gave equally conclusive results. It requires a little more chloride of zinc, in consequence of the large quantity of water which it contains or produces.

Oleic Acid.—300 parts of oleic acid from a candle factory where the lime saponification is practised, treated when hot with 12 per cent. of anhydrous chloride of zinc, furnished on distillation a solid white product weighing 170, and fusible at 89°·6 F., and a yellow product of butyraceous consistence weighing 60. This is a remarkable fact, and clearly shows the similarity of the action of chloride of zinc and sulphuric acid. By means of sulphuric acid, 25 to 30 per cent. of solid fatty matter is obtained by distillation from oleic acid produced in the manufactories of candles where lime-saponification is practised.—*Comptes Rendus*, February 21, 1859, p. 410.

New Process for depriving Spirit of Fusel Oil. By M. Breton.

This new process is merely an application of a well-known principle, upon which depends the operation by which bromine contained in saline solutions is separated by æther. The spirit containing fusel oil is mixed with a body which is insoluble, or but sparingly soluble, in alcohol, but which can dissolve fusel oil.

For this purpose olive oil is employed. A few drops of this are poured into a bottle with spirit containing fusel oil, which is then shaken, left to settle, and decanted. This process, notwithstanding its simplicity, is not applicable to the treatment of large quantities of spirit or low wines.

The author first made use of a filter consisting of disks of woollen stuff, slightly soaked in oil, and held between two perforated plates of metal. The spirit was deprived of fusel oil, but only until the woollen cloth was saturated with the volatile oil, when it absorbed no more. By means of a current of steam at a pressure of two or three atmospheres, the wool could be readily freed from the volatile oil; but the exposure to steam at this temperature rendered the wool useless for a repetition of the process. The woollen stuff consequently had to be given up, and after many trials it was replaced by a layer of powdered pumice-stone, which acts exactly in the same way as the woollen stuff, but without losing its power of absorption when exposed to a temperature necessary for the volatilization of the fusel oil.—*Moniteur Industriel.* Dingler's *Polytechn. Journal*, cl. p. 429.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Occurrence of Quercitrine as a Colouring Matter in Flowers. *By* F. Rochleder.

Quercitrine, discovered by Chevreul in the bark and albumen of *Quercus tinctoria*, prepared pure by Bolley, and the nature of which was ascertained by Rigaud, is contained not only in the above-mentioned North American oak, but also in some other plants. Rutine or rutic acid, discovered simultaneously in the leaves of *Ruta graveolens* by Weiss and Kümmel, and more accurately investigated by Bornträger, was discovered by Hlasiwetz and the author in the flower-buds of *Capparis spinosa*, and by Stein in the so-called Chinese yellow berries, which, according to Von Martius, are the undeveloped flower-buds of *Sophora japonica*; and Hlasiwetz has since ascertained the identity of rutine and quercitrine.

Quercitrine therefore is a common constituent of *Quercus tinctoria* (bark and alburnum), *Ruta graveolens* (leaves), *Capparis spinosa* (flower-buds), and *Sophora japonica* (undeveloped flower-buds). To these four plants the author adds a fifth, the Horse-chestnut (*Æsculus Hippocastanum*).

The fully-developed leaves of the latter tree contain quercitrine, although not in any considerable quantity. In the bark of the stem and twigs, in the scales of the leaf-buds, in the undeveloped leaves still enclosed in the buds, the author could detect no quercitrine. The yellow fallen leaves were investigated for quercitrine by Norbert Duras. He found in them only traces of this body. He obtained only ½ grm. from several large baskets of the leaves.

As constituents of the ripe seeds, Fremy describes saponine, a crystalline bitter matter, and a yellow colouring matter. The yellow colouring matter, which is separated with difficulty from the preponderating quantity of other constituents, is quercitrine. The author has prepared pure quercetine from it.

If the cotyledons of the ripe seeds be cut into thin slices, treated with alcohol of spec. grav. 0·853, and left standing for 8 or 10 days in a closed vessel, a golden-yellow tincture is obtained; the colour of this is due to quercitrine, the only coloured constituent of the

cotyledons, which, after extraction, appear perfectly white. With the exception of quercitrine, the seed lobes contain no single one of the peculiar constituents of the bark, leaves, &c. of the plant; all these must consequently be produced from the constituents of the seed during the process of germination.

The flowers of the horse-chestnut, when just unfolded, are colourless with a yellow spot. In 24 hours the yellow colour passes to red. All dropped flowers have red spots. As of two flowers standing quite close together in the thyrsus, one is always evolved about a day sooner than the other, we always see a flower with a yellow spot standing next to one with a red spot. 174 pounds of dropped flowers were extracted with alcohol of spec. grav. 0·853; the decoction was filtered through linen, then through paper, and set to cool. Crystals of a wax separated, and were collected on a filter. The filtrate was distilled on the water-bath, in order to recover the greater part of the alcohol. The residue of distillation mixed with water, separated into two strata; the lower one formed a mass of greenish-brown resin, and the upper was of reddish colour, and could be easily separated from the resin. With solution of acetate of lead it gives a yellow precipitate, soluble for the most part in acetic acid. The portion not soluble in acetic acid contains some of the resins, which are not quite insoluble in the fluid in question. The solution in acetic acid, which was filtered from the insoluble compounds of the resins with oxide of lead, as well as the fluid which had been filtered from the precipitate produced in the original fluid by neutral acetate of lead, gave a chrome-yellow precipitate with basic acetate of lead. These two precipitates also contain a small quantity of compounds of lead and resin, and a very minute quantity of a pectine body, whilst they contain a considerable amount of quercitrine and a little quercetine. From the abovementioned quantity of flowers the author obtained about half an ounce of pure quercetine. From this it follows that quercitrine and quercetine occur as colouring matters of flowers.

Quercitrine is formed in the leaves, after they have burst forth from the buds, whilst æsculine disappears from them; this substance passes from the bark into the bud scales, and from these into the young leaves during their evolution, where it furnishes the material for the formation of quercitrine. The quercitrine of the leaves becomes in part a constituent of the seed lobes, but a part of it is removed with the falling flowers. Quercitrine thus stands in the same position with pinipicrine, which was found by Kawalier in the bark of *Pinus sylvestris*, and which also occurs in that of the horse-chestnut. Kawalier has shown that this substance splits into sugar and an ætherial oil of the camphene group, which becomes resinified with the greatest facility. A portion of this resin is exsuded upon the scales of the buds. The remainder falls off with the flowers.

Quercitron bark is still the best material for the preparation of quercitrine or quercetine. The method by which these two bodies may be cheaply prepared is as follows:—

The bark is put into a kettle, and sufficient water is poured over it to cover it to a depth of several lines. The water is boiled, and the boiling solution strained through linen. The residue is then pressed, and the decoction set to cool. The bark is then again decocted with the same quantity of water. The first decoction deposits a considerable quantity of impure quercitrine, but the second deposits little or none. The quercitrine is collected upon a filter of fine linen, and allowed to drain. The filtrate is mixed with muriatic acid, which produces a voluminous flocculent fawn-coloured precipitate, which soon settles to the bottom, its flakes at the same time becoming smaller. The precipitate is removed by filtration, and the filtrate, which contains quercitrine, is heated in the water-bath with constant stirring, as long as the amount of quercetine separated increases; it is then filtered whilst hot through paper. Quercetine remains upon the filter. The subsequent deposit from the filtrate is very small in amount and impure, so that it is best to throw it away.

Both the quercitrine and quercetine are now purified by trituration with a little alcohol of spec. grav. 0·853, and heating on the water-bath. The heated mass is placed upon a linen filter, and pressed after the fluid has drained off. A small quantity of quercetine or quercitrine with a great amount of impurities pass into the alcohol. The extracted mass is dissolved in boiling alcohol, the solution is filtered while hot, and boiling water is added to it until a distinct turbidity makes its appearance. After it has cooled a few degrees, the principal portion of the colouring matter separates. It is collected upon linen filters, and pressed. By repeating this process several times, the substances are obtained nearly pure. The greater part of the alcohol used is recovered by distillation on the water-bath. In this way, which is not very expensive, a hundred weight of the bark furnished quantities of quercitrine and quercetine, which render it possible to investigate these bodies more accurately.—*Sitzungsbericht der Akad. der Wiss. zu Wien*, xxxiii. p. 565.

On Œnantholosulphurous Acid. By D. Mendelejef.

By the action of chloride of barium upon a solution of pure œnantholosulphite of soda, $C^{14}H^{13}NaS^2O^6+2H^2O^2$, a white precipitate is obtained, as has already been indicated by Bertagnini. When weak solutions are mixed, this precipitate appears in the form of crystalline, shining scales; but strong solutions furnish an amorphous mass. The precipitate is but sparingly soluble in water. The analysis of this baryta-salt gave,—

	Calculated.		Found.	
Carbon	34·219		34·1	34·2
Hydrogen ..	5·296		5·3	
Barium	27·896	27·9	28·5	27·6
Sulphur....	13·035		13·0	
Oxygen....	19·554			

When this baryta-salt is treated with an equivalent proportion of dilute sulphuric acid, and left standing for a few days at the ordinary temperature, the precipitate contains an intermixture of sulphate of baryta, whilst a mixture of sulphuric acid and œnantholosulphurous acid remains in solution.

The latter is produced by double decomposition—

$$2(C^{14}H^{13}BaS^2O^6 + H^2S^2O^8 = 2(C^{14}H^{13}HS^2O^6) + Ba^2S^2O^8.$$

The presence of œnantholosulphurous acid in the solution is proved by the formation of the crystalline soda-salt (characterized by its small solubility in water, alcohol, and especially in saline solutions) by the action of concentrated solutions of NaCl, $Na^2S^2O^8$ and $Na^2C^2O^6$. A double decomposition is produced by these:—

$$C^{14}H^{13}HS^2O^6 + NaCl = C^{14}H^{13}NaS^2O^6 + HCl.$$

The crystals formed dissolve when slightly heated, increase in size on cooling, and possess generally all the properties of the salt obtained by Bertagnini. This salt, purified by crystallization, gave on analysis 9·5 and 9·6 of sodium, and 35·5 per cent. of carbon, corresponding with the formula $C^{14}H^{13}NaS^2O^6 + H^2O^2$.

A purer œnantholosulphurous acid may be prepared by conducting sulphurous acid into a vessel containing water and œnanthole, when the latter combines with sulphurous acid,

$$C^{14}H^{14}O^2 + S^2O^4 = C^{14}H^{14}S^2O^6,$$

and the œnantholosulphurous acid produced dissolves in water. With a concentrated solution of chloride of sodium, this solution forms œnantholosulphite of soda (analysis gave 9·8 and 9·7 per cent. of sodium). Free muriatic acid may easily be detected in the filtered fluid.

The acid could not be obtained free from water, as its solution is decomposed into œnanthole and sulphurous acid when heated, and even when evaporated under the bell of the air-pump.

Œnantholosulphurous acid dissolves hydrated oxides of zinc and copper, displaces carbonic acid, sulphuric acid, and muriatic acid from the solutions of their soda-salts, forming $C^{14}H^{13}NaS^2O^6 + 2H^2O^2$. With salts of potash and ammonia (except the carbonates) it does not readily enter into double decomposition, for $C^{14}H^{13}KS^2O^6 + 2H^2O^2$ and $C^{14}H^{13}(NH^4)S^2O^6$ crystallize with far more difficulty than $C^{14}H^{13}NaS^2O^6 + 2H^2O^2$. Œnantholosulphurous acid and the solutions of its salts form precipitates in solutions of salts of baryta, lead, lime, and strontia.

Probably all the aldehydes of the monobasic acids, $C^{2n}H^{2m}O^{2p}$, are capable of forming similar aldehydosulphurous acids, $C^{2n}H^{2m}S^2O^{4+2p}$. The author has already obtained benzoaldehydosulphurous acid.

The existence of the aldehydosulphurous acids in some degree confirms the analogy of the reactions between the aldehydes and the alcohols, for the aldehydosulphurous acids are in the same relation to the aldehydes, as the æther acids to the alcohols. For example, as we obtain from $C^4H^6O^2$—$C^4H^5HS^2O^8$, we also obtain

from $C^{14}H^{14}O^{2}$—$C^{14}H^{13}HS^{2}O^{6}$. Both acids are monobasic, and are obtained from bibasic acids and organic compounds. The compounds obtained by Bertagnini are nothing but alkaline salts of such aldehydosulphurous acids.—*Bull. de St. Pétersb.*, xvii. p. 350.

On the Reduction of the Chlorides of Barium, Strontium, and Calcium by Sodium, and on Alloys of these Metals. *By* H. Caron.

Hitherto magnesium is the only earthy metal whose chloride has been reduced by sodium. The author has succeeded in reducing the chlorides of barium, strontium, and calcium by the following process:—

The presence of a foreign metal in the fused salt in which the reduction takes place often facilitates the operation, either by uniting the molecules of the reduced metal, if it be capable of being dissolved, or by localizing the action of the reducing metal previously alloyed.

The author commences by preparing alloys of sodium with different metals, such as lead, tin, bismuth, antimony, &c. These alloys are generally prepared with ease, but often with a violent evolution of heat and light, which necessitates the employment of certain precautions in their preparation. To render these alloys tractable, they should not contain more than one-third of their weight of sodium.

To reduce chloride of barium, strontium, or calcium, it is sufficient to fuse it in an ordinary crucible, and to add to it, when the chloride is perfectly fluid and quite red, one of the alloys of sodium. It is then heated for a few moments to enable the metal to collect, and then taken from the fire. The crucible must contain an excess of chloride in proportion to the sodium employed. A crystalline metallic ingot is obtained, having a peculiar aspect according to the alloyed metals. These compounds only contain traces of sodium when they are properly prepared. The analyses of some of them gave,—

Lead and calcium.		Antimony and calcium.		Bismuth and barium.	
Calcium.....	17·10	Calcium....	7·60	Barium..	28·00
Lead	81·10	Antimony	92·40	Bismuth	72·00
Sodium	0·32				
Silicium and tin	0·52				
Magnesium ..	0·38				
Loss	0·58				

When the amount of sodium employed exceeds a certain limit, the proportionate quantity of metal reduced is diminished.

These alloys may also be obtained by a single operation and without the use of sodium. To prepare an alloy of tin and barium, for example, it is sufficient to form an intimate mixture of carbonate of soda, charcoal, chloride of barium, and tin in powder, and to heat it until no more vapours of sodium are evolved. The reaction is easily understood.

These alloys, however prepared, are true compounds, which are

not destroyed by heat. Thus an ingot of bismuth and barium placed in a charcoal crucible and heated to the temperature of fusion of nickel, lost very little in weight; a small quantity of barium was destroyed by the oxide of carbon which is always present in the atmosphere of crucibles. All the alloys become oxidized rapidly in the air, and decompose water very briskly when they contain more than 5 per cent. of the earthly metal; they then leave the foreign metal not acted upon in the state of a black powder.

The alloys of barium, strontium, and calcium with antimony, when placed in water, evolve a hydrogen containing much antimony. Although it contains a certain excess of hydrogen, produced by the alloy of calcium, the gas gives on analysis 1·768 gr. of antimony for each litre of gas produced by the decomposition. The alloys with bismuth do not furnish hydrogen combined with that metal.

A mixture of chloride of calcium and sodium, in such proportions that there may be a great excess of sodium, when fused in a *closely covered* iron crucible, care being taken not to raise the temperature beyond that of the volatilization of sodium, furnishes an alloy of sodium and calcium, which parts with the whole of its sodium by distillation in an iron vessel. The calcium, however, is left in the state of sponge, which is oxidized so energetically that the metal cannot be fused without destroying it almost entirely. The lime which surrounds the calcium is also an obstacle to the union of the metallic particles, but it is probable that by improving the process it may be isolated in a pure state. The employment of the same means to obtain alloys of sodium with barium and strontium led to no result.—*Comptes Rendus*, Feb. 28, 1859, p. 440.

On the Preparation of Anhydrous Sulphuric Acid. By M. Osann.

Nordhausen sulphuric acid has a spec. grav. of 1·856 and only boils at 550° F. The consequence of these two properties is that in the reoccupation of the space formed at the bottom of the retort by the vapours of the acid, a percussion takes place which may easily break the retort.

To prevent such an accident, the author made use of a well-known means, consisting in the introduction of a coiled up platinum wire into the acid. It is necessary that one end of the wire should touch the bottom of the vessel, and the other project above the surface of the fluid. By this means the distillation of sulphuric acid may be effected over an Argand lamp without any danger.

In this case the author remarked that the distillate contained a much larger quantity of anhydrous sulphuric acid than is obtained by distillation without the platinum wire.

The receiver was placed in a water-bath at 50° F. White flakes were then seen in the distillate; they gradually increased, and it was observed that about half the acid became consolidated into a white mass of anhydrous sulphuric acid. If the receiver be taken

out of the water-bath and exposed to the air, a portion of the distillate evaporates, whilst the rest solidifies to anhydrous acid. The author makes the following remarks in explanation of this fact.

The boiling-point of a fluid depends partly upon its individual nature, partly upon the pressure of the atmosphere, and lastly, in part upon the pressure exerted by superior strata of fluid upon the lower ones, supposing the heat to be applied from below. If the uppermost stratum of the fluid be brought to the boiling-point, there is only the pressure of the atmosphere to be overcome; but if, on the contrary, the lowest stratum be heated to boiling, the pressure of the upper strata is to be overcome besides that of the atmosphere. The fluid must, therefore, in this case, boil at a higher temperature; but if there be in it a coiled platinum wire, passing from below upwards, the heat will be conducted from the bottom to the superior strata, and the uppermost stratum will boil sooner than the lowest. Now it is evident that as oil of vitriol is a mixture of anhydrous and hydrated acid, and the former boils at a lower temperature than the latter, the anhydrous acid will carry over more of the hydrated acid with it when the distillation is carried on at a high temperature, than when it is effected at a lower one. If, therefore, the uppermost stratum boils, comparatively very little of the hydrated acid can be carried over. The author, however, thinks it not improbable that the catalytic action of the platinum may have something to do with the effect produced.—*Verhandl. der Würzburger phys.-med. Gesellsch.*, October 30, 1858.

On some Modified Results attending the Decomposition of Bituminous Coals by Heat. By Dr. A. A. Hayes.

When bituminous coal is exposed in proper vessels to a gradually increasing temperature, at a certain point decomposition commences and continues, while heavy hydrocarbon vapours, mixed with the vapours of water and salts of ammonia, escape, and may be condensed.

The proportion of permanent gases formed is small in comparison with the weight of the liquids produced, when the decomposition of the coal is carefully regulated.

In the ordinary rapid breaking up of the composition of coal by heat suddenly applied in the manufacture of illuminating gas, the proportion of permanent gases is increased, but the heavy fluid hydrocarbons are also formed. This mode of decomposition is evidently a mixed one partaking of the characters of a regulated distillation, while at the same moment a more complete destruction of the coal is proceeding in some parts of the mass.

A further decomposition of the fluid products, condensed from either or both of these modes of operating, takes place when we again subject them to the influence of heat; and this well-known fact is the basis on which improvements in the manufacture of illuminating gas have been founded,—a secondary destruction of vapours being effected in appropriate apparatus heated to a high temperature.

This character, which all the bituminous coals exhibit, of passing into carbon nearly free from vapours only when heavy fluid hydrocarbons are also formed, has, in a chemical view, been the strongest fact adduced in opposition to the generally-received opinion that the anthracites and semi-anthracites have resulted from chemical changes of bituminous coal, through the agency of the heat of igneous rocks which have disturbed their beds. The heavy hydrocarbons, represented by ordinary coal-tar, are the most indestructible bodies known; and wherever anthracites exist, we should expect to find near by those products of the chemical changes effected in the coal. Such is the delicacy of the balance existing between the elements of the heavy hydrocarbons, that no second distillation of them can be effected; they always undergo decomposition by heat, with the separation of carbon, which, under any known natural conditions, would remain to attest their previous presence.

Considerations of this kind have led me to experiment on the changes which coals undergo by heat, where the influencing conditions were not the same as those usually seen; and the results of extended trials demonstrate that the bituminous coals may be broken up into permanent gases, vapours of water, and ammoniacal salts, while carbon remains as a fixed product.

If we substitute, for the ordinary forms of apparatus used in decomposing coal by heat suddenly applied, any modification of form which compels the gas, as it forms, to escape from the more highly heated part of the mass of coal through a small opening, or, better, a small eduction-pipe, the heavy hydrocarbons do not form part of the products which escape. Generally the light, nearly colourless oils of the benzole series appear with the aqueous solutions of the ammoniacal salts, while only an accidental quantity of carbon is deposited in the eduction-pipe. The carbon left is more than usually compact and hard; and such coals as ordinarily produce much water when they form heavy hydrocarbons, afford less than half the usual amount when thus decomposed under the influence of the constant presence of an atmosphere of permanent gases.

In following the observations at the earlier stage, it was found that the size of the eduction-tube leading the gas from the hotter part of the mass of coal undergoing changes, exerted a most marked effect on the composition of the products. It was established as a fact, that in an ordinary coal-gas retort, the size of the conduit might be varied so as to allow the tar-like bodies to form, or to prevent their appearance at pleasure.

But a more remarkable result was obtained, when, after having prevented the production of heavy hydrocarbon fluids, the influence of reduced size of tube was studied in its relation to the composition of the gas afforded by a particular kind of coal. To a certain extent, the chemical constitution of the gas formed was found to be under control, and the conclusion reached was, that dissimilar permanent gases may be thus obtained from the same parcel of coal without a modification of temperature.

Any explanation of the change of composition induced in the

volatile parts of bituminous coals under the above-described conditions should not include mechanical pressure, which is no greater than often exists in ordinary cases.

It seems probable that the presence of an atmosphere of nearly permanent gases in the decomposing vessel, and the regular continuous flow of them from the coal, prevent the formation of heavy vapours at the instant of change in the coal. In support of this point, we find the temperature necessary to convert coal into gas without the presence of heavy hydrocarbons much less high than when they are produced.

We may therefore observe the decomposition of coal without the simultaneous formation of tar, and *beds of coal may be converted under existing natural conditions to anthracite, without secondary products being formed.*—Silliman's *American Journal* for March 1859.

Note on the Production of the Hydrosulphocyanic Æthers.
By M. Schlagdenhauffen.

Sulphocyanide of æthyle may be obtained by passing a current of chloride of æthyle into a hot alcoholic solution of sulphocyanide of potassium. The decomposition does not take place rapidly, and requires the action of the sun's rays. From this it might be foreseen that by employing iodide of æthyle in place of chloride, the same result should be attained, and this is proved by experiment. The decomposition must be effected in a sealed tube, and the mixture, when heated to 212° F. in the water-bath, begins to deposit cubical crystals upon the walls of the tube in about a quarter of an hour; 2·91 grms. of sulphocyanide of potassium and 4·62 grms. of iodide of æthyle were heated to 212° F. for two hours. The tube was cooled and broken at its upper extremity, and the whole of the liquid distilled by keeping the tube in a chloride of calcium bath. The product of the distillation was sulphocyanide of æthyle, characterized by its peculiar odour. On treating this distilled liquid with an alcoholic solution of sulphuret of potassium, and evaporating it to dryness, long needles of sulphocyanide of potassium, colouring salts of iron blood-red, were obtained.

The residue in the tube was carefully taken up with water and treated with acetate of lead. The yellow precipitate of iodide of lead weighed 6·81 grms., corresponding with 4·80 grms. of iodide of potassium, instead of the calculated quantity, 4·82 grms. Notwithstanding this small error, we may assume that sulphocyanide of potassium is entirely decomposed by iodide of æthyle at 212° F. in a sealed tube.

Two analogous experiments made with iodide of methyle and amyle, showed that under the same conditions the su phocyanide was decomposed, and gave origin to sulphocyanides of methyle and amyle, together with iodide of potassium.

Sulphocyanide of barium gave the same result. The tube was heated o 248° F.; it was covered internally with large crystals. It

was cooled, opened, and distilled; the distilled liquid was hydrosulphocyanic æther, and the residue in the tube was iodide of barium. Two other experiments showed that the iodides of amyle and methyle act in the same way as iodide of æthyle.

The same decompositions were obtained with metallic sulphocyanides, and notwithstanding the comparative insolubility of these salts, the author proved the formation of their iodides and of the hydrosulphocyanic æthers. Thus by treating 2·68 grms. of sulphocyanide of silver, together with alcohol, with 3·08 grms. of iodide of æthyle to 320° F. for two hours in the oil-bath, the white salt became yellow. The liquid formed is sulphocyanide of æthyle dissolved in alcohol, and the insoluble compound iodide of silver.

Sulphocyanide of lead is transformed with equal facility. Crystallized iodide of lead of a fine yellow colour is formed, and the liquid in the tube, after treatment with sulphuret of potassium and evaporation, furnishes fine needles of sulphocyanide of potassium.

Sulphocyanide of mercury presents some peculiarities. This salt, mixed with alcohol, and heated in a sealed tube with iodide of æthyle, furnishes a red deposit and a yellow liquid. When the liquid in the tube is distilled, it furnishes hydrosulphocyanic æther, but only in small quantity. Moreover, the yellow liquid, when concentrated, deposits pretty prismatic needles, which probably are a compound of iodide of mercury and sulphocyanide of æthyle. The iodides of methyle and amyle behave similarly.—*Comptes Rendus*, February 14, 1859, p. 331.

On two New Derivatives of Saccharic Acid.
By Professor Heintz.

When dry gaseous ammonia is passed through a solution of saccharic æther in æther, which may contain alcohol but no water, saccharamide is formed. A precipitate is produced consisting principally of saccharamide, but also containing saccharate of ammonia, because it is impossible in this operation to exclude every trace of water. By washing the precipitate first with æther and then with cold water, saccharamide is obtained pure in the form of a white amorphous powder, which, when moist, renders red litmus-paper slightly blue, dissolves without change in lukewarm water, and crystallizes from the solution on cooling. If it be dissolved in boiling water, it is converted into saccharate of ammonia. Saccharamide does not dissolve in æther. Boiling alcohol, on the contrary, takes some of it up, but a portion of this separates on cooling in small crystals. When heated, saccharamide becomes yellow, brown, and finally black, diffusing an odour of burning nitrogenous substances. The remaining coal at last burns away without residue when heated to redness. Hydrate of potash slowly evolves ammonia from saccharamide in the cold, more rapidly when heated. Acids, on the contrary, convert it immediately into the ammoniacal salt of the acid employed, and into saccharic acid.

Analysis of saccharamide lead to the empirical formula $C^6 H^4 NO^6$.

Heintz regards it as most probable that the rational formula of this body is $N \left\{ \begin{matrix} C^{12} H^{3} O^{12} \\ NH^{4} \end{matrix} \right.$, so that it is an ammonia in which 2 equivs. of hydrogen are replaced by the bibasic saccharyle ($C^{12} H^{3} O^{12}$), and the third by ammonium.

The second new derivative of saccharic acid is a compound of saccharate with chloride of lead, which is obtained when the precipitate produced by a soluble neutral saccharate in solution of chloride of lead, is dissolved in a large quantity of a boiling solution of chloride of lead so weak that no chloride separates from it on cooling, and the filtered fluid is left to cool. Small crystalline laminæ separate; these are nearly insoluble in cold water, and dissolve with but little more facility in boiling water, whilst they are readily soluble in dilute nitric acid. When dried, the compound consists of a white nacreous powder, which when heated becomes brown and black, and lastly deposits metallic lead. It contains no water of crystallization, and its composition may be expressed by the formula $(C^{12} H^{8} O^{14} + 2PbO) + 2PbCl$.—*Ber. der Akad. der Wiss. zu Berlin*, 1859, p. 13.

ANALYTICAL CHEMISTRY.

Analysis of Commercial Stannate of Soda.
By William Wakefield, *Glasgow**.

Several methods are in use for estimating the amount of tin in this commercial salt.

The process usually employed is to precipitate the tin by sulphuretted hydrogen and estimate it in the form of sulphide, but as stannate of soda often contains notable quantities of arsenic, this process is manifestly inapplicable in such cases, as both tin and arsenic would be thrown down.

Another process is to estimate the tin in the form of stannic acid, precipitating it by dilute sulphuric acid, and calculating the metallic tin from the precipitate obtained. This method, however, is objectionable when arsenic is present, in consequence of the formation of an insoluble arseniate of tin.

These processes may be easily and accurately performed with pure stannate of soda, but when applied to samples containing arsenic, it is necessary to remove this substance before the tin can be determined.

Levol's process for separating arsenic from tin consists in placing a certain quantity of the salt in a glass tube, heated to redness, and passing over it a current of hydrogen gas, by which the tin is left in the metallic form, and the arsenic is sublimed in the tube. The extreme tediousness of this method, however, prevents its general application to commercial analysis.

After an extensive trial of these and other processes, I am led to recommend the following method, based on Reinsch's well-known

* Communicated by the Author.

process for the detection of arsenic, as both convenient and accurate for the estimation of tin in stannate of soda containing arsenic acid.

A convenient quantity of the sample in fine powder, say 25 grains, is dissolved in a flask with a small quantity of water and ½ an ounce of pure hydrochoric acid. Several slips of copper-foil are successively added, and the mixture boiled till all the arsenic is separated from the solution, which is known by the copper last added retaining its natural colour, and not becoming coated with arsenic even after protracted boiling.

The solution, after the separation of the copper and arsenic by filtering, is then gently heated with slips of sheet zinc, and the precipitated tin dissolved in boiling hydrochloric acid. In carrying out the last operation, great care must be observed to ensure perfect solution of the tin, which is always mixed with a small quantity of precipitated copper.

The complete solution of the tin is known by the precipitate acquiring the red colour of metallic copper. The solution is then filtered, and the amount of tin determined by Dr. Penny's process for the analysis of protochloride of tin (Quarterly Journal of the Chemical Society, vol. iv. p. 239). The following are some of the results obtained by this process. The stannate of soda used was in large and well-defined crystals, and was perfectly free from arsenic. The amount of tin in it was estimated by reducing in the usual manner with nascent hydrogen, and adding afterwards bichromate of potash.

1st experiment.	2nd experiment.	3rd experiment.
31·5	31·8	31·2

Several experiments were then made, in which a known quantity either of arsenious acid or arseniate of soda was mixed with the stannate, and the tin estimated without separating the arsenic. The results in every instance exceeded the actual amount of tin present, and corresponded to the quantity of arsenic added. Similar experiments were then carried out in which the arsenic was removed by the copper process here suggested, previous to the estimation of the tin. I obtained as follows:—

1st experiment.	2nd experiment.	3rd experiment.
31·4	31·5	31·2

These results leave no doubt that this method is well adapted for the valuation of commercial samples of stannate of soda.

Glasgow, April 14th, 1859.

A Method of Estimating the Nitrous Acid contained in the Nitrous Vitriol obtained from Gay-Lussac's *Nitre Recovering Apparatus.* *By* Peter Hart*.

Having for some years employed at these Works Gay-Lussac's process for recovering the nitrous gas of the vitriol chambers,

* Communicated by the Author.

I have long sought for an easy and convenient method of estimating the quantity of nitrous acid contained in the nitrous vitriol. My first idea was to convert this NO^3 into NO^5 by the addition of a permanganate, but in this I was not successful. I then tried if it was possible to avail myself of the action of NO^3 on hydriodic acid; for this purpose I added a measured quantity of the nitrous vitriol to a solution of iodide of potassium, mixed with starch-water, adding after this a normal solution of protochloride of tin until the blue colour produced disappeared; but this process I found gave nothing but discordant results. I almost despaired of effecting my object, until I happened to see Schwarz's method of analysing the nitrites*: I found that I could adapt this to my purpose. It is well known that NO^3 and urea, when brought into contact, decompose each other.

$$C^2 N^2 H^4 O^2 + 2NO^3 = 2(CO^2) + N^4 + 4(HO).$$

In my first experiments I weighed the evolved gases, employing for this purpose a modification of Fresenius and Will's carbonic acid apparatus; this consisted of two small flasks and a larger one connected together; a measured quantity of the nitrous vitriol was placed in one of the smaller flasks, a solution of urea in the larger; into this the nitrous vitriol could be sucked over, the evolved gases being forced through some strong sulphuric acid contained in the third flask; the apparatus being weighed before and after the evolution, the difference of course was the weight of the gases given off. This process, though not difficult, could, I found, be simplified. It is easy to see that if a normal solution of urea could be added from a burette to a measured quantity of the nitrous vitriol until the NO^3 in the latter was decomposed, an easy method presents itself; but this is not practicable:—first, because it is not easy to procure quantities of pure urea; and secondly, supposing this got over, the nitrous compound is so unstable, that the CO^2 and N given off carry with them a considerable quantity of NO^3, as was apparent from the smell, thus vitiating the result; eventually I surmounted both difficulties by employing nitrate of urea, and reversing the above process. Nitrate of urea, being a crystallizable body, is easily obtained in a state of purity; I add nitric acid to a solution of crude urea, collect the crystals, wash, drain, and dry them at the temperature of the air. The mode of proceeding is as follows:—first, a test-solution is prepared by dissolving 5 or 6 grains of iodide of potassium in about 2 ounces of starch-water; a white plate is dotted over with spots of this solution; 20 grains of nitrate of urea are then weighed out, put into an evaporating basin with from 2 to 2½ ounces of water, and the whole heated to boiling; an ordinary burette is then filled up with the nitrous vitriol to be tested; the gas flame beneath the basin is lowered so as to keep the contents just below boiling; if this is not attended to, the nitrous gas is given off immediately it touches the solution and before it can act on the urea; the nitrous solution in the burette is now poured into the basin drop by drop, a copious evolution of gas ensues; during this addition the contents

* Chemical Gazette, vol. vii. p. 279.

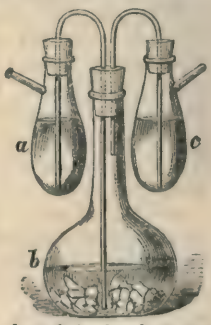
of the basin must be continually stirred, and a drop carried by the glass rod to one of the drops on the plate; this must be often repeated until a drop from the basin colours one of the spots on the plate blue: this indicates the completion of the process. The rationale of this latter part of the process is, that all the urea being decomposed, free NO^3 remains in the liquid; this of course, on coming into contact with the iodide of potassium, sets iodine free, which immediately combines with the starch, forming iodide of starch, and producing the blue colour. The calculations are not difficult. 123 parts, or 1 equiv. of nitrate of urea, are decomposed by 2 equivs. or 76 parts of NO^3, representing 108 parts of dry nitric acid, NO^5, or 170 parts of nitrate of soda. Therefore, supposing 25 alkalimeter measures have been taken to decompose the 20 grs. urea, it is evident that these 25 measures contain as much NO^3 as the 20 grs. of urea could decompose, that is, 12·35 NO^3, representing 17·56 NO^5, or 27·64 NaO,NO^5: now as there are 7000 alkalimeter degrees in a gallon, it is easy to find how much nitrate of soda a gallon of the nitrous vitriol represents; this, multiplied by the number of gallons in the cistern, gives the whole nitrate of soda recovered. Or, let a represent the number of measures employed, b the nitrate of soda represented by the 20 grs. nitrate of urea, c the number of alkalimeter divisions in a gallon, and d the number of gallons in the cistern; then

$$\left.\frac{b \times c}{a}\right\} \times d = x.$$

Ardwick Bridge Chemical Works, Manchester.

A Modification of Fresenius *and* Will's *Apparatus adapted to the Examination of Limestones, &c.* *By* Peter Hart*.

Whilst making some experiments detailed in a previous paper, I contrived an apparatus which, I think, would be found useful in the determination of carbonic acid in limestones, and in all cases where sulphuric acid as a decomposer is objectionable. Perhaps no piece of apparatus employed in chemical research has undergone so many modifications, but in almost all sulphuric acid has been used to decompose the carbonate; now sulphuric acid often, as in the case of carbonate of lime, forms an insoluble sulphate, which encloses the particles of carbonate, and either retards or entirely suspends its own action. In the apparatus about to be described, hydrochloric acid is used as the decomposing agent, which obviates this difficulty. The figure needs little description: the fragment of limestone to be analysed is broken up into pieces sufficiently small to enter the neck of the larger flask, is



* Communicated by the Author.

weighed, and put in with a little water; the small flask *a* is filled with HCl, and the third flask *c* with strong sulphuric acid; a little pellet of wax is placed on the end of the small tube inserted into the neck of the small flask *a*. The whole is weighed; the siphon is set going by sucking at the tube inserted into the neck of the small flask *c*; when sufficient has come over, the small tube on flask *a* is again closed with its wax stopper; the evolution of gas commences; if more HCl is required, the wax stopper is again removed; when the carbonate is dissolved, the CO^2 is either sucked or blown out, and the apparatus again weighed.

Carbonate of baryta could be analysed by means of this apparatus; and I think it would be found useful in the testing of guano by Dr. Davy's method, the weighed guano to be placed in the flask *b*, the hypochlorite of soda in flask *a*; the same manipulation would be required as has been just detailed.

Ardwick Bridge Chemical Works, Manchester.

Determination of the Amount of Carbon in Limestones.

By C. Brunner.

It may sometimes perhaps be of geological interest to determine the amount of carbon in limestones. The following method is founded upon the well-known circumstance that carbon is converted into carbonic acid by the simultaneous action of chromate of potash and sulphuric acid.

A weighed quantity of the stone under examination is broken up into pieces of the size of peas, and treated with dilute sulphuric acid, care being taken to employ a considerable excess of the latter, and the fluid is finally heated. The solution with the residue is poured into a cylindrical glass, and after the insoluble portion has settled, it is washed by repeated decantation. The residue is then poured into a flask, and a little sulphuric acid is added to it. To 100 grms. of water covering the residue, about 15 grms. of sulphuric acid are added. The flask is then furnished with a gas-tube, the descending limb of which dips into a small bottle containing a clear mixture of solution of chloride of barium and ammonia, and placed, for refrigeration, in a vessel of water. The contents of the flask are then boiled. If a perceptible turbidity be produced in the small bottle, which would indicate a residue of carbonic acid, the boiling is continued until a fresh test-fluid is not rendered turbid. From 2—3 grms. of crystallized bichromate of potash are then put into the flask, the gas-tube is again inserted, and the fluid is boiled for at least half an hour. The carbonic acid evolved is then obtained in the bottle in the form of carbonate of baryta.

To determine the quantity of the precipitate, the bottle is carefully closed at the conclusion of the operation, until the precipitate is completely deposited at the bottom; it is then washed repeatedly by decantation, and finally on a filter, dried, and calcined.

When the operation is properly performed, the flask contains either no insoluble residue, or only one which from its colour and

appearance, cannot be supposed to contain any carbon. The latter is usually the case. If there be any doubt upon this point, the fluid may be again boiled and the gas conducted into a fresh test-fluid of ammonia and chloride of barium.

As, in these investigations, the amount of carbon found is usually very small ($\frac{1}{1000}$th or even less), it is advisable to use rather large quantities of material, such as 100 grms.—Dingler's *Polytechn. Journal*, cl. p. 377.

PROCEEDINGS OF SOCIETIES.

Royal Institution of Great Britain.

Friday, March 25, 1859.

"On the Estimation of the Organic Matter of the Air." By Robert Angus Smith, Esq., Ph.D., F.R.S.

After describing the opinions concerning organic matter in the air, and the various attempts made to estimate the amount, the lecturer described a method of obtaining the relative quantity by means of mineral chameleon, permanganate of potash or soda. This mineral had been proposed by Forchammer as a mode of estimating the organic matter in water, but it was capable of estimating quantities much more minute. At first the air was passed through the solution of chameleon, but this was not found to cause complete action. It was necessary that the air should remain for some time in contact with the solution to be decomposed. It was then ascertained that the relative amount of organic and other oxidizable matter in air could be found by a simple metrical experiment in a few minutes.

The lecturer then said:—In working out this idea, it has been found that a vessel of the capacity of 80 to 100 cubic inches is the most convenient. This is equal to rather less than a quart and a half, and rather more than a litre and a half.

The solution of chameleon used must be extremely weak, so that small quantities cannot readily be distinguished by gaslight. 600 grains of it are required to decompose 5 grains of a standard solution of oxalic acid. The standard solution of oxalic acid is so made that 1000 grains neutralize 1 grain of carbonate of soda. A thousand grains contain therefore 1·184 grain of crystallized oxalic acid.

To prepare the solution, a manganate was formed by heating nitrate and carbonate of soda and manganese, assisted by a little chlorate of potash. There was the most minute trace of nitrate remaining in the solution. Perhaps chlorate of potash would have been better, but I had no idea at the time of the difficulty afterwards found in obtaining the same quality. A solution of this manganate was made in pure water, and carbonic acid passed through until a reddish purple shade was obtained. It was then tested by oxalic acid, adding three or four drops of pure sulphuric acid. The purest water obtainable was added to dilute it to the proper amount.

This often failed; and I have sometimes for a whole week failed to obtain the proper solution. Although I call it permanganate, it is not entirely so; it is a mixture of manganate and permanganate. A permanganate of the strength described has a dingy appearance and uncertain colour. I do not doubt that a pure permanganate of a suitable strength may be obtained pleasant to work with. There is some difficulty in obtaining pure water for preparing the solution. If allowed to stand for some time with a manganate it becomes purified.

The solution of chameleon is apt to change, although slowly, even when it is hermetically sealed in a glass tube. The solution described had become nearly colourless when sealed up hermetically for about three months. It is found readily to change when it is exposed to air by frequent removal of the stopper of the bottle containing it. Its strength must be tested occasionally; and if it differs from the standard, a calculation must be made for its reduction. The strength of the permanganate solution is extremely small. A few grains of the ordinary solutions of manganese used will make some thousand grains of the solution here employed. The reason of this lies in the extremely small amounts of organic matter found in even the worst air.

The vessel used is simply a bottle with a perforated stopper, through which pass two tubes. To one of these a stopcock is attached, to the other a clasp or stopcock. The standard size proposed is 100 cubic inches; and to this all the experiments have been reduced; the vessels actually used contain between 80 and 100 cubic inches of air. The stopcock is of glass, or of hard caoutchouc, which is still better. When the bottle is to be filled with the air to be tested, the stopper is removed, and the pipe of an exhausting pump is inserted, reaching to the bottom of the bottle. The pump is made like a cylindrical bellows of about 8 inches long when stretched out, and about 4 in diameter, and is compressible into the thickness of about 2 inches. The sides are made of thin Mackintosh cloth. By the use of the pump the air of the vessel is removed, and the external air of course enters. A few strokes of the pump are sufficient, *i. e.* from 6 to 10. After ten strokes I perceive no change, and am inclined to think that it is an unnecessary number. The test liquid is poured into a graduated tube or burette, containing somewhat more than will be required. A portion is then poured into the tube which passes through the stopper, and the stopcock is opened to allow it to pass. Small quantities are used; when it has entered the bottle, the liquid is made to spread over the sides, and time given it to be exposed to the action of the air; it is found that in five or six minutes a decided epoch is attained from which to date the comparative action.

In order to see the colour the liquid must be allowed to trickle down the sides of the vessel, and collect itself at one point of the circumference at either end of the cylindrical part of the bottle. This part must be raised up to the level of the eye, so that the longest axis may be presented to the sight, and thereby the deepest shade

of colour. It requires some time to accustom oneself to the sight of such a small amount of colour; but when it is once well observed, it will be found to be a method which will admit of the greatest precision. The first few drops which are poured in will probably be decolorized at once: a few drops more must then be added; if they become decolorized, a few more must be used; and so on until there is a perceptible amount of colour remaining. When this occurs, the experiment is concluded. The amount of the reagent used is then read off from the graduated measure. If the liquid be of the proper strength, and the bottle the required size, the number of grains gives the comparative quantity at once. Sometimes the amount of organic matter is so small that there is no appreciable action, on even the smallest amount of solution by one vessel of air. In this case it is necessary to fill the bottle several times. The mode of doing this is apparently extremely rude, but the results are such as not to demand a finer method at present. A finer method, of course, would need little ingenuity to contrive. At present I merely remove the stopper and fill again with air as before. During the period of filling the vessel the surface of the liquid is reduced to its smallest amount, and the change it undergoes is either inappreciable, or so constant as not to affect the results.

In analysing the air in this manner, it is found that a decided result is attained in about five minutes. Sometimes the result is decided in one; that is, there is a termination to the rapid action. This peculiarity is probably to be explained by the following experiments. If we pour decomposing matter on the permanganate solution, it is rapidly destroyed. If the matter be not in a state of decomposition, the action is much slower.

These different results promise a mode of dividing the organic matter of the air into classes according to its quality. These facts are mentioned merely as germs of a future inquiry. In large towns, where coals containing much sulphur are burnt, the sulphurous acid takes the oxygen of the chameleon, and an apparently large amount of organic matter results. This sulphurous acid is of itself an impurity, perhaps as hurtful as some kinds of organic matter.

We measure by this means the amount of oxygen needful for the oxidizable matter of the atmosphere, and all such matter is impurity, in some places entirely organic, in others, such as towns, mixed with inorganic gases.

Some of the principal results obtained by this method were as follows:—

*Relative quantities of Organic and other oxidizable Matter in the Air of**

Manchester (average of 131 experiments).....	52·9
„ All Saints, E. wind (37 experiments).....	52·4
„ „ W. wind, less smoky (33 expts.)	49·1

* A few of these results were published in the 'Athenæum' during last summer The present numbers are somewhat higher, being reduced, for the sake of uniformity, to correspond to a vessel of 100 cubic inches.

Manchester, All Saints, E. wind, above 70° F. (16 exp.)	58·4
„ „ „ below 70° F. (21 exp.)	48·0
„ In a house kept rather close	60·7
In a pigstye uncovered	109·7
Thames at City, no odour perceived after the warmest weather of 1858	58·4
Thames at Lambeth	43·2
„ Waterloo Bridge	43·2
London in warm weather (six experiments)	29·2
„ after a thunder-storm	12·3
In the fields S. of Manchester	13·7
„ N. of Highgate, wind from London	12·3
Fields during warm weather in N. Italy	6·6
Moist fields near Milan	18·1
Open sea, calm (German Ocean, 60 miles from Yarmouth)	3·3
Hospice of St. Bernard, in a fog	2·8
N. Lancashire	about same
Forest at Chamouni	2·8
Lake Lucerne	1·4

The first experiments undertaken were in Manchester, and the average amount obtained was in the city about 50, gradually diminishing in moving towards the country until it was found in the fields at 13; on passing a sewer stream about a mile from the outskirts, the amount rose to 83. The atmosphere on the Thames was not measured whilst at its worst, but immediately afterwards; when, however, it had ceased to affect the senses of most persons at least, the amount was very high, viz. 58. I was anxious to know how far the Thames affected the atmosphere of London, and tried some experiments: the result was that the influence appeared to cease almost immediately; the fact of a block of houses standing in the way was enough to prevent the influence; when at the worst this may not have been the case; to arrive at the other side of the block, the vapour would generally require to rise high, so that it would become mixed with a great deal of air. The amount obtained in a few trials in the streets of London was 22 to 34; going on to Highgate, the numbers sank from 33 to 24; on descending the north side of Highgate Hill a distinct change was perceived, the numbers being 18; the wind meantime was blowing from the city: the few experiments made in the fields in summer gave 10 to 12. The numbers 6 to 18 were obtained in Switzerland and Lombardy. The moist fields around Milan gave 18; when the water passes off the rice fields, producing the unhealthy season, I do not doubt that the amount will be much higher. It was not convenient for me to stay, nor to go farther to places distinctly infected with malaria. I was desirous of trying it in some of the hovels of the Vallois and the Val d'Aosta, but the weather being fine, and the people living much out of doors, the inquiry was not encouraging. The few experiments made did not give very striking results, whereas the lower parts of our own towns gave results most decided: I imagine the cause of this to be that a drier air does not allow the offensive matter to rise so readily.

This fact has many ramifications, but it will explain several difficulties in our sanitary science. It is with the assistance of moisture that the organic matter is conveyed into the air.

Moisture itself, as may be supposed, does not produce any action on the test; one of the lowest numbers obtained was on the German Ocean, about 60 miles from land; the day was calm and clear. In the straits of Dover, when the wind was blowing briskly from the German Sea, the amount obtained was very high, but as there was a slight spray the experiments were disregarded. About 8000 feet high on the Alps, a dense fog showed also one of the smallest amounts obtained; the ground was entirely bare rock, and could not give out organic matter. The amount was 2·8.

The influence of height was very decided; in the higher grounds of Lancashire, near Preston, the numbers being from 2 to 4. A wind blowing down from the Mer de Glace gave rather more than at a lower point, although coming down the hill; a dry pine forest in the neighbourhood, although very fragrant, did not appear to raise the number. The influence of the sea and of height seem equally decided.

A few hasty experiments made in the hothouses at Kew led me to believe that there was less increase there than might have been expected, the amounts obtained being less than in London, but more than outside the houses, where it was cooler. At the same time weeks or months should be given, when only hours were allowed for the experiments.

The influence of heat appears to be to increase the amount, when there is moisture present.

The influence of dryness seems to be towards diminishing the amount.

The influence of great cold has not been tried yet.

The influence of rain in hot weather, to some extent of course a cooling influence, but chiefly a means of washing the air, seems most decided. After a thunder-storm and shower at Camden Square, the number, which was previously 31, fell to 12.

The influence of our towns, especially our smoky towns, is most decided also; it is easy to tell by this test, when in the outskirts of a town, whether the wind is blowing from the town or the country.

A distinct difference was always found between the front and back of Manchester houses: a similar difference obtained when a room had been inhabited for some time, and the difference was of course very marked when the smell of a sewer came into the house. I had a good opportunity of observing this in my laboratory last year.

It must be remembered that the numbers given for some places were obtained on one day of the year only, and we must be careful not to draw too many conclusions: we have yet to learn what kind of organic matter is wholesome and what is unwholesome. I believe that this is the next great point to be attended to; at present we are only becoming able to ascertain the gross amount. I feel this caution to be needful, lest the numbers should be used to prove too much.

THE CHEMICAL GAZETTE.

No. CCCXCVIII.—May 16, 1859.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Contributions towards the Knowledge of the Compounds of Vanadium. *By* A. Schafarik.

The material from which the author prepared the compounds of vanadium investigated by him, was obtained by Patera from the pitchblende of Joachimsthal. The author procured it from Wöhler, at whose disposal the Academy of Vienna had placed a portion of the material prepared by Patera. The investigation was carried on in Wöhler's laboratory.

The author makes the following observations upon the preparation of the raw material. In the first place, Patera roasted the ore with carbonate of soda and nitrate of potash, precipitated the arsenic acid from the solution by magnesia salts, and then the vanadic acid by muriate of ammonia. Subsequently, however, he found it easier to slightly acidulate the extract of the roasted ore with muriatic acid, mix it with decoction of galls, and precipitate impure tannate of vanadium by neutralization with carbonate of soda. A portion of the author's material consisted of shining black amorphous fragments, which contained much water and organic matter; this was evidently the precipitate with tannic acid, simply dried. Another portion consisted of hard, grayish-blue lumps, part dark, part light, and still containing carbon; this was the preceding substance calcined. A third portion, marked as impure vanadiate of soda, was a grayish-yellow powder, which, after fusion with carbonate of soda and nitrate of potash, appeared almost undiminished, and then only contained carbonate of lime, alumina, and oxide of iron, so that it was probably at first impure vanadiate of lime.

All three portions were worked up in the same way. The substance was mixed with its own weight of a mixture of equal parts of nitrate and carbonate of soda, and introduced in small quantities into a red-hot iron crucible, heated until it was fused, poured out,

pounded, and boiled with water until it was dissolved. The dark brown deposit contained iron, manganese, copper, alumina, and lime; the solution contained arseniate, molybdate, tungstate, and vanadiate of soda; it was much concentrated and saturated with muriate of ammonia (in fragments). In a few days the vanadiate of ammonia was as completely precipitated as possible; the fluid was decanted, the precipitate washed with solution of muriate of ammonia and alcohol, dried, and calcined. In this way it always happened, that, with small quantities of crude solution, the precipitation of which was soon completed, the vanadiate of ammonia turned out pure white, and when heated furnished readily fusible vanadic acid, solidifying in a beautiful crystalline form; whilst when larger quantities were precipitated, the salt had a yellowish colour, and when ignited did not furnish a red powder, but a brown infusible one. The cause of this was the tungstic acid, which at first forms a very soluble neutral ammoniacal salt, but then passes into the acid salt ($3\,NH^4O, 7\,WO^3$, Lotz), which of itself is difficult of solution, and dissolves with still more difficulty in solution of muriate of ammonia, and consequently mixes with the precipitate. The readily soluble molybdate of ammonia is not precipitated by muriate of ammonia, so that it remains in the mother-liquor. This also contains vanadiate of ammonia, which is not completely precipitable by muriate of ammonia, and also tungstate and molybdate of ammonia; it is simply evaporated to dryness, and the residue heated in a closed crucible until the volatilization of all the muriate of ammonia. By lixiviation all the molybdenum, tungsten, and vanadium are obtained in the form of a gray powder, a mixture of oxides and nitrurets. The author obtained from his materials at least twice as much tungstic and molybdic acid as vanadic acid. For the purification of the crude vanadic acid he found two means,—either extraction by caustic ammonia, and renewed precipitation of this solution by muriate of ammonia, by which a dazzling white, perfectly crystalline vanadiate of ammonia resulted; or repeated continued digestion with (a little) dilute sulphuric acid at a boiling heat, as long as the sulphuric acid was still coloured. By this means there was produced a fine reddish-brown solution of sulphate of vanadic acid ($VO^3, 3SO^3$, Berzelius, Fritzsche), and there only remained a mixture of tungstic acid and oxide of tungsten. The solutions might be directly evaporated to dryness, and the residues ignited; the author preferred converting them into sulphate of vanadium by oxalic acid, evaporating them until the free sulphuric acid began to be volatilized, cooling them, pressing the bluish-green crystalline paste of sulphate of vanadium, washing it with alcohol, and igniting it. (The separation of vanadium from tungsten is very accurately effected in this way, and might perhaps be employed quantitatively.) From the mother-liquor of the sulphate, oxide of vanadium is thrown down by alkalies, and this is also converted into vanadic acid by ignition with nitric acid. In this way the author obtained in all about 30 grms. of pure acid. with which he made his experiments. Subsequently he obtained a purer acid by decomposing perchloride of vanadium

with water; this, when fused, shot into radiate crystalline needles of 30—40 millims. in length, and 2—3 millims. in breadth, but furnished no measurable crystals. The colours of vanadic acid, which have never been accurately described, present an extraordinary resemblance to those of croconate of copper, except that the brown fundamental colour is more reddish, and, like the metallic-adamantine blue surface-colour, much deeper than in the croconate. The powder is of a dingy rust colour (ochreous); on the other hand, by the evaporation of solutions of nitrate of vanadium, a powder of an intense tile-red colour, perhaps amorphous acid, is obtained.

The author has also determined the density and the atomic volume of vanadic acid; he found it in two experiments (with 2·7 and 1·4 grm.) =3·472 and 3·510 at 68° F., therefore on the average 3·491. The acid prepared from pure perchloride, and beautifully crystallized, was finely powdered and extracted in the pycnometer. As vanadium, in most of its chemical relations, appears to be intermediate between tungsten and molybdenum, it was to be supposed that the three homologous acids of this group would have the same atomic volume.

Now, according to Karsten, tungstic acid possesses the atomic volume $\frac{116}{7\cdot14}=16\cdot2$. For the density of molybdic acid we have only the antiquated statement of Bergmann (3·46), which is evidently much too low, as it makes the atomic volume $=\frac{70}{3\cdot46}=20\cdot3$. The author therefore undertook two determinations with very beautifully crystallized and finely powdered acid; these gave the numbers 4·423 and 4·370 at 68° F. The latter number is more accurate, and gives the atomic volume $\frac{70}{4\cdot37}=16\cdot0$, consequently in good accordance with tungstic acid. On the other hand, the above-mentioned density of vanadic acid gives its atomic volume at $\frac{92\cdot5}{3\cdot491}=26\cdot5$, therefore quite different from the preceding. But then this number agrees exactly with the atomic volume of the triatomic oxygen compounds of the arsenic series, as shown by the following summary:—

		Density.	Atomic volume.
Arsenious acid	AsO^3	3·72—3·70 Karsten	26·6—26·7
Oxide of antimony	SbO^3	5·56 Mohs	25·9
Oxide of bismuth	BiO^3	8·174 Karsten, 8·97 Boullay	28·4—25·9

We have therefore the remarkable fact that the specific volume of vanadic acid (and also that of the metal, as is subsequently shown) places the compounds of vanadium in a different position from that indicated by the other analogies (especially the typical formulæ of the compounds), removing them, namely, from the tungsten into the arsenic group. This circumstance is rendered more interesting by the fact that the native vanadiate of lead is isomorphous with the

analogous salts of the pentatomic acids of the arsenic series, namely campylite and pyromorphite. Kenngott, as is well known, has deduced from this, as also from the loss of 3·21 per cent. in Rammelsberg's analysis of the vanidinite of Obir, that we must assume in this mineral the presence of a pervanadic acid, VO^5; but without taking into consideration that isomorphism and analogous constitution are not necessarily connected, as is proved by calc-spar and nitrate of soda, arragonite and nitrate of potash, permanganate of baryta and sulphate of soda, and many other compounds, and without taking into account that the above-mentioned loss is completely explained by Rammelsberg's own observation, Briegleb's remarkable double salts, $NaF + PO^5, 3\,NaO + 24\,HO$, and $NaF + AsO^5, 3\,NaO + 24\,HO$, which are isomorphous with alum, $NaO, SO^3 + Al^2O^3, 3\,SO^3 + 24\,HO$, present a phenomenon which tells strikingly upon our case, namely isomorphism of sulphates (triatomic acids) and phosphates (pentatomic acids). The atomic volume of vanadic acid also furnishes an easier explanation:—The atomic volume of anhydrous arsenic acid, according to Karsten, is $\frac{115}{3{\cdot}734} = 30{\cdot}8$, a number which does not differ more from the atomic volumes of arsenious acid and vanadic acid (26·5—26·7) than the atomic volumes of decidedly related bodies; and as the isomorphism of the native vanadiate of lead with the above-mentioned minerals is mere homœomorphism, we cannot expect any equality of their atomic volume either in the whole or in their constituents. The near concordance of the atomic volumes of vanadic and arsenic acids, combined with the fact of Briegleb's salts, doubtful as may be all conclusions, even in the case of solid bodies, drawn from the specific volume of the constituents as to that of the whole, certainly furnishes an explanation of the isomorphism of vanadinite with the apatite group, which is simpler and more in harmony with the facts than Kenngott's assumption.

The preparation of the perchloride of vanadium from the acid, which for this purpose need not be perfectly pure, is a tolerably simple and easy operation. The acid, reduced to the finest powder and mixed with its weight of lamp black, is ignited in a tube of hard glass, in a current of dry hydrogen gas, then the hydrogen is expelled by carbonic acid, and lastly, dry chlorine gas is passed through the tube at a dull red heat; the perchloride is produced with the greatest facility, and condenses in the colder part of the tube. This is drawn out in a point, which is connected by a cork with a U-tube, cooled in water, snow, or ice; in order to lose none of the substance, which is extremely volatile in the stream of gas, the vapours evolved are conducted into water or dilute ammonia. The U-tube rapidly fills with a liquid, which appears nearly blood-red by the separation of amorphous vanadic acid, in consequence of unavoidable traces of moisture, and fumes violently when exposed to the air. Berzelius expelled the absorbed chlorine by a stream of air; the author found rectifications more convenient; he distilled the crude product (on the oil-bath) through an elbowed tube drawn out into a capillary point, into strongly refrigerated glass

tubes, which were immediately sealed hermetically. The preparation by gently heating protoxide of vanadium (VO) in gaseous chlorine, when it splits into pure fused vanadic acid and perchloride of vanadium, is convenient:—$3VO + 6Cl = VO^3 + 2VCl^3$. The author has prepared the chloride in this way and ascertained by analysis its identity with that prepared from protoxide of vanadium and charcoal; for from the complicated relations of the oxychlorides of tungsten and molybdenum, it would have been almost a matter of course to seek an oxychloride in the perchloride prepared in the second way.

Perchloride of vanadium is a clear and exceedingly mobile golden-yellow fluid, which fumes violently in the air, and diffuses dense clouds of amorphous vanadic acid, of a cinnabar-red colour; when mixed with a little water, it becomes thickish and blood-red, and when heated, of a fine blue from formation of the chloride, VCl^2; with much water it gives a clear pale yellow solution, which, on evaporation, leaves red pulverulent vanadic acid without becoming blue.

Its boiling-point is 260°·6 F.; the author determined this with 10 grms. of pure distilled substance. The bulb of the thermometer was half immersed in the fluid, and the mercury stood, during the brisk ebullition, firmly at 257°·9 F. until the last drop was evaporated. In the oil-bath he had previously found the boiling-point nearly 18° F. too high, notwithstanding every precaution. The vapour of the perchloride is of a pure and intense yellow colour, like that of chlorine. The density of perchloride of vanadium was found in two experiments (with 6·6 and 6·1 grms. of substance) to be 1·763 and 1·765 at 68° F., mean = 1·764; hence the atomic volume $= \frac{175}{1{\cdot}764} = 99{\cdot}2$. No comparison is possible with the homologous perchlorides of tungsten and molybdenum, as these are unknown, but a comparison may be made with the triatomic chlorides of the arsenic group. We know from Kopp's classical investigations that the atomic volumes of fluids are only strictly comparable at their boiling-points, and unfortunately no attempt has been made to investigate the expansion of perchloride of vanadium by heat in order to calculate therefrom its atomic volume at the boiling-point; nevertheless a glance at Kopp's last Table is sufficient to indicate a remarkable circumstance which enables us to fill up this gap, namely that the fluid volatile chlorides of simple radicals of approximately similar boiling-points expand almost equally in equal intervals of time (from 32° F. to their boiling-point) without reference to their molecular composition. The numbers may speak for themselves:—

Protochloride of sulphur..	S^2Cl	boiling-point	264°·2 F.	Kopp.
Perchloride of tin	$SnCl^2$	„	239° F.	Pierre.
Perchloride of titanium ..	$TiCl^2$	„	276°·8 F.	„
Protochloride of arsenic ..	$AsCl^3$	„	273°·2 F.	„
Protochloride of antimony	$SbCl^3$	„	433°·4 F.	Kopp.

Expansion from 32°—264°·2 F.=0·159 (of the volume at 32° F.)
" " 32°—239° F.=0·154 " " "
" " 32°—276°·8 F.=0·155 " " "
" " 32°—273°·2 F.=0·152 " " "
" " 163°·4—433°·4 F.=0·144 " " 163°·4 F.)

We may therefore be allowed to reduce the density of the perchloride of vanadium by the expansion of protochloride of arsenic at 32° and 260°·6 F.; it is then at 32°=1·799, and at 260°·6=1·573, and consequently the atomic volume of the perchloride of vanadium at its boiling-point $=\frac{175}{1{\cdot}573}=111{\cdot}2$. If we bring together herewith the atomic volumes of the chlorides of the arsenic group at their boiling-points according to Kopp, we have

for PCl = 93·9
" $AsCl^3$ = 94·8
" $SbCl^3$ = 97·7 (Sb=122)
" VCl^3 =111·2,

according to which the atomic volume of the perchloride of vanadium certainly differs too much even from the highest member of the group, protochloride of antimony, to allow the assumption of a relationship; nevertheless the difference only amounts to 0·14 of the whole; and an increase of the atomic volume with the atomic weight is also unmistakeable in other series, so that even in the perchloride of vanadium we cannot overlook an approximation to the molecular character of the arsenic series.

A number not less interesting than the atomic volume was the density of vapour of the perchloride of vanadium; the author determined this by the method of Dumas, as he had not the apparatus of Gay-Lussac and Natanson, but in order that he might not waste the valuable substance he proceeded as follows. The chloride was introduced as rapidly as possible by a capillary funnel into the thoroughly dried balloon, the neck of which was already elbowed (at an acute angle), but not drawn out to a sharp point; the elbow-tube was then united by a cork with a well-cooled U-tube, and immersed as deeply as possible (the balloon downwards) in an oil-bath, which was gradually brought to the desired temperature; after this had remained at the same point for some time, the horizontal arm of the elbow-tube was sealed before the blowpipe. The author then weighed the balloon with vapour, and empty after opening, cleaning, and drying. The data are as follows:—

Weight of the balloon with vapour ..... =22·435
" " " air ..... =21·875
Temperature of the bath on sealing..... =+476°·6 F.
Height of barometer on sealing ..... =748 millims.
" " " weighing..... =744½ "
Temperature..... =+66°·2 F.
Volume of the balloon ..... =184·8 cub. cent.
Residue of air ..... =2·0

From this we obtain the density of vapour=6·41; and as $\frac{175}{6·41}$=27·3, it follows, according to Kopp's simple rule, that 1 atom of perchloride of vanadium in the condition of vapour occupies 4 vols. If we calculate the density of vapour theoretically from this, we obtain $\frac{175}{28·88}$=6·06, a deviation from observation which on the one hand is insuperable, as we had only to decide here between 1, 2 and 4 vols., and, on the other, is exactly on the side where it must have been expected, because where the elbow-tube of the balloon lay in the bracket, some fluid chloride was condensed, and could not by any means be driven off. Even this result is interesting, in so far as it proves the rule that all volatile inorganic trichlorides give 4 vols. of vapour (the rule applies to BCl^3, PCl^3, PO^2Cl^3, $AsCl^3$, $BiCl^3$, VCl^3, and also to the corresponding bromides and fluorides, whilst the bichlorides, in the hitherto usual expression of their formulæ, like the mono- and sesqui-chlorides, fill 2 vols. with their vapour—$SiCl^2$, $TiCl^2$, $SnCl^2$, $ZrCl^2$; S^2Cl, CrO^2Cl, $HgCl$; Al^2Cl^3, Fe^2Cl^3). This rule, which is certainly empirical, might allow us to refer bodies of doubtful relations to their proper place in one or other series. Take, for example, the question whether tantalum and niobium are biatomic radicals (H. Rose), or triatomic (Berzelius), or sesquiatomic (Hermann), in other words, whether they belong to the tin or tungsten group. The atomic volume of the metallic acids of the tin series is 10 to 11, as shown by the following numbers :—

SiO^2 =11·3 Dumas.
TiO^2 9·8—9·6 Mohs (Rutile).
SnO^2 11·3 Berzelius.
TaO^2 11·0 H. Rose (calcined in the porcelain furnace, Ta=69).
NbO^2 14·1 H. Rose (calcined in the porcelain furnace, Nb=49).

If Ta=103, and tantalic acid=TaO^3, the atomic volume=16·7 would be very accordant with that of tungstic and molybdic acids (16·0—16·2). Indeed, all the compounds of tantalum too strongly indicate its biatomic nature to leave any doubt upon the subject; on the other hand, the deviation of niobium is at least not unfavourable to a doubt in this direction. A determination of the density of vapour of perchloride of tantalum, and also of both chlorides of niobium, as also a determination of their atomic volumes, would be of great interest, and probably not very difficult.

As the analysis of the perchloride of vanadium by Berzelius gives a loss of chlorine of 3 per cent., and the possibility of the presence of oxychlorides was not excluded; the author analysed the chloride by dissolving in water a portion weighed in a glass bulb, acidulating it with nitric acid, and precipitating the chlorine as chloride of silver. A separate portion dissolved in water, evaporated, and calcined, gave vanadium (as acid)—

	Found.			Calculated.		
V	38·9			1 = 68·5		39·14
Cl	..	61·52	61·32	3 106·5		60·86

From the manifold analogies with chromium on the one hand, and with tungsten and molybdenum on the other, it occurred to the author to attempt the preparation of an oxychloride of vanadium. The method which, with chromium, leads so quickly to the object, namely, distillation of a fused mixture of bivanadiate of soda and chloride of sodium with fuming nitric acid, gave nothing:—the mixture became brown, gave off traces of vapour of perchloride, but soon became green, and then contained only a salt of oxide of vanadium. Heating oxides of vanadium in gaseous chlorine also furnishes only perchloride, whilst with tungsten and molybdenum numerous oxychlorides are thus formed. If there really exists no oxychloride of vanadium, this is a further analogy with the arsenic group.

The perbromide of vanadium (VBr^3) is produced exactly like the perchloride; it is solid, very deliquescent, readily volatilizable, appears to evaporate before fusion, and sublimes in beautiful long, scarcely transparent needles, of a deep greenish brown body colour, and metallic adamantine superficial lustre. Its further investigation will be the subject of a future memoir.

Vanadic acid may be reduced to the metallic state by ignition in hydrogen. The acid was placed in a tray, which was pushed into a gun-barrel, and the latter exposed to a strong red heat in a blast-furnace for two hours, whilst hydrogen was passed through it.

The reduction is most easily effected by the method employed by Von Uslar for the preparation of tungsten and molybdenum, namely, by the passage of dry hydrogen charged with vapour of perchloride of vanadium through red-hot glass tubes. The author put 10 grms. of perchloride into a U-tube which lay upon a wire grating, and the beak of which opened through a cork into a hard glass tube, wrapped round with sheet metal, and maintained at a red heat in a Liebig's combustion furnace. A rapid stream of hydrogen flowed through the apparatus and carried the vapours of the perchloride with it; the evolution of the latter being regulated by means of one or two fragments of hot charcoal. The escaping muriatic acid and the excess of vapour of perchloride were conducted into water. When the operation was concluded the water was green, and a quantity of extremely light micaceous scales of a fine brownish-red colour and strong lustre floated in it; these, when separated by filtration and rapidly dried in the air, soon deliquesced into a dark green mass. The tube itself was clothed throughout nearly its whole length with a deep iron-grey crust, of a brownish metallic lustre, specular against the glass, crystalline within, which could only be partially detached from the glass, because the latter had itself become rough and crystalline in parts. Only the hindmost part of the tube, which had suffered least from the heat, was coated with a white, crystalline, translucent crust of a fatty lustre, which, by long exposure to the air, deliquesced into a blue fluid. On the other hand, the whole tube, especially in the half that had been least heated, was filled and almost stuffed with a loose aggregation consisting partly of large, shining, black crystalline laminæ, and partly and principally of a dark greyish-brown

powder, with a slight metallic lustre; the latter contained the large brownish red scales sparingly scattered in it. Both the loose powder and the dark crusts are metallic vanadium. The crust for the most part falls to powder in its removal from the tube, and this powder is exactly similar in appearance to the mass deposited in a pulverulent state; both were extracted with water in order to remove any traces of soluble chloride, but only the metal deposited in a pulverulent form gave a green colour to the water (probably by the solution of the intermixed red laminæ, which are perhaps VCl, and the white substance, forming a blue fluid by deliquescence, VCl^2). After extraction, both substances form a crystalline powder which sinks rapidly in water, and has a brilliant metallic lustre and fine dark brown colour; when heated in contact with air, they both acquire a blue tint, then smoulder away to form protoxide, and slowly deliquesce to pure vanadic acid. The rapidity with which this metal is acted upon by nitric acid is remarkable; if only a few drops of nitric acid be added to hot water in which the metallic powder is lying, a brisk evolution of gas commences immediately, and in a few minutes the metal is entirely dissolved in the form of beautifully blue nitrate of vanadium. The metal reduced by hydrogen also, and (according to Johnston) that fused in a charcoal crucible, are violently dissolved by nitric acid, whilst tungsten and molybdenum, whether reduced by hydrogen or by carbon, resist the strongest acids. 1·82 grm. of pulverulent metal (reduced from VCl^3 by H), when oxidized by concentrated nitric acid (which took place with a sort of explosion), gave 2·43 grms. of pure fused vanadic acid, which is an increase of weight of 33·5 per cent., whereas pure metal requires 35·0 per cent. The density of the metal in a crystalline powder was found by the author (but only with not quite 0·5 grm.) at 68° F.=3·64. From this we obtain the atomic volume $\frac{68·5}{3·64}=18·8$, consequently nearly equal to the mean of the atomic volumes of the arsenic group (P=16·8; As=13·3; Sb=17·9; Bi=21·9), which amounts to 17·8 and requires a density of vanadium of $\frac{68·5}{17·8}=3·84$, near enough to the number found, when we consider the uncertainty of the latter (about +0·1). On the other hand, the difference from the atomic volume of tungsten and molybdenum, which amounts to 5·3 as the mean of both (molybdenum $\frac{46}{8·62}=5·34$, Buchholz; tungsten $\frac{92}{17·5}=5·26$, as the mean of all statements), is very considerable, so that here also the great departure of vanadium from its previous neighbours, as well as its agreement with the arsenic group, becomes remarkable; for with the atomic volume 5·3 it ought to have the density $\frac{68·5}{5·3}=12·93$, and, like tungsten, be one of the heaviest metals, whereas in reality it is one of the lightest. That, however, the above number cannot be very incorrect for the density of vanadium, is proved by the following consideration:—

in the monoxides of most of the heavy metals, according to Kopp, the atomic volume of the oxide is equal to that of the metal + 2·6; the atomic volume of oxide of antimony likewise is equal that of antimony + 3 times 2·5; that of oxide of bismuth (according to Karsten) equal that of bismuth + 3 times 2·4. If we assume this proportion also in the case of vanadic acid, we obtain V = 26·5 − 3(2·6) = 18·7, a number which accurately corresponds with the one found.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xxxiii. p. 1.

Note on the Action of Nitric Æther upon Iodide of Potassium. By E. Juncadella.

The action of nitric æther upon iodide of potassium is very complex; amongst other products hydriodic æther and a little ordinary æther are formed.

Equivalent proportions of iodide of potassium and nitric æther, mixed with their volume of alcohol, were put into a tube and sealed up, and then heated to 212° F. for 15 hours; the tube, opened after cooling, evolved a small quantity of gas, and contained a liquid strongly coloured by free iodine. By distilling it, hydriodic and ordinary æther were separated.

The ordinary æther appears to result from the action of the hydriodic æther upon alcohol in an acid liquid, in accordance with the experiments of Reynoso. The gaseous products and the free iodine are also due to some secondary reaction produced by the oxidizing action of the nitric acid.

The reaction which furnishes hydriodic æther is a new example of slow decomposition between a salt and an æther; it is represented by the equation

$$C^4H^5O,NO^5 + KI = C^4H^5I + KO,NO^5.$$

Comptes Rendus, February 14, 1859, p. 345.

On the Behaviour of the Chlorides of Sulphur towards Amylic Alcohol. *By* L. Carius *and* E. Fries.

Carius some time since studied the behaviour of chloride of sulphur towards salts, hydrated acids, and æthylic alcohol. The following results were obtained by the continuation of this investigation. The authors operated first with the brown chloride of sulphur, which is not a simple chemical compound of chlorine with sulphur, but probably a mixture of the chloride S^2Cl^4, representing sulphurous acid, but which has not yet been isolated, and the so-called di- or semi-chloride of sulphur, S^4Cl^2; they also employed the latter alone. The behaviour of chloride of sulphur towards amylic alcohol is exactly analogous to that with ordinary alcohol.

1. *Brown Chloride of Sulphur* especially acts violently upon amylic alcohol; currents of muriatic and sulphurous acids are evolved, so that whilst the mixture is being effected, the materials must be kept cool, and provision must be made for the condensation and return of the volatilized portions. The authors employed

a proportion of 90 parts of amylic alcohol to 200 parts of brown chloride of sulphur saturated with chlorine at a low temperature.

After the completion of the mixture a clear yellow fluid was produced, which was almost entirely freed from absorbed muriatic and sulphurous acid gases by a gradual application of heat, by which the temperature was raised to 214° F. The residue was separated into two parts by distillation.

The first portion passing at 230° F. was chloride of amyle, still retaining a little intermixed semichloride of sulphur. After purification, about 100 parts of pure chloride of amyle were obtained; calculation requires 110 parts. Analysis showed it to be pure chloride of amyle; its boiling-point, determined and corrected by the method described by Kopp, was 213°·62 F. as found by Kopp.

The portion afterwards passing (at 302° F. without blackening) was semichloride of sulphur.

Brown chloride of sulphur therefore converts amylic alcohol into chloride of amyle, leaving semichloride of sulphur, and perhaps forming a small quantity of chloride of thionyle. Leaving out of consideration the semichloride of sulphur and chloride of thionyle, the decomposition is

$$S^2Cl^4 + 2.\left.\begin{matrix}C^{10}H^{11}\\H\end{matrix}\right\}O^2 = 2ClH + 2.\left.\begin{matrix}C^{10}H^{11}\\Cl\end{matrix}\right\} + S^2O^4.$$

2. *Semichloride of Sulphur*, by its action upon amylic alcohol, furnishes, together with chloride of amyle and a small quantity of amylomercaptan,

$$\text{Amylosulphurous æther } \left.\begin{matrix}S^2O^2\\(C^{10}H^{11})^2\end{matrix}\right\}O^4,$$

which, when pure, is a colourless, thick, oily fluid, with an odour resembling at once amylic alcohol and æthylosulphurous æther. In moist air it evolves sulphurous acid and passes through all shades of colour from pale red to dark brown; considerable quantities of sulphuric acid may be detected in a fluid that has undergone this decomposition. By agitation with water, especially when heated, only a small quantity of sulphurous acid is produced, but the æther is decomposed into amylic alcohol and amylosulphurous acid. The same products are formed during the very rapid decomposition by alkalies, except that sulphurous acid is almost entirely wanting.

When quite pure, the æther undergoes no change by heating to 302° F.; at a higher temperature it becomes brown, and evolves sulphurous acid and some amylic alcohol; at 392° F. the fluid begins to boil and distils over, the boiling-point constantly rising until it exceeds 482° F., with almost complete decomposition into amylic alcohol and sulphurous acid. In a current of a neutral gas, on the contrary, the whole of the pure fluid distils over, for the most part unaltered at a temperature of 446°—482° F.

For the preparation of this æther, the semichloride of sulphur must be mixed directly with an excess of amylic alcohol. After long digestion, the evolution of gas ceases, and the fluid becomes

nearly colourless. This fluid must not, however, be distilled directly, because otherwise scarcely any sulphite of amyle distils without decomposition. The fluid is left standing for a long time at a low temperature in a carefully closed vessel; it is then poured away from the deposit of dirty brown sulphur, and distilled. Chloride of amyle first passes, then the excess of amylic alcohol, after which the boiling-point of the residue rises rapidly. Even at 302° F. the residue begins to grow brown, and it is necessary to carry on the distillation in a carefully dried stream of hydrogen gas, as otherwise nearly all the æther is decomposed.

The crude product thus obtained at above 392° F. contains sulphite of amyle mixed with much amylic alcohol, produced by decomposition during the distillation; this fluid must be protected from the air, rapidly washed with a very dilute solution of carbonate of soda, and then with much water, in order to remove the amylic alcohol and sulphurous acid.

The product is different when equivalent proportions of semichloride of sulphur and amylic alcohol are mixed together. If this mixture be digested until there is no longer any evolution of muriatic and sulphurous acids, for which at last a temperature of 230° F. is necessary, a yellow fluid is obtained, with separated, semifluid sulphur under it. If the yellow fluid be distilled immediately, chloride of amyle is obtained; the boiling-point then rises very rapidly to 464° F. and higher, when the residue becomes almost entirely carbonized with evolution of products containing sulphur, with a disgusting odour, and much sulphurous acid.

If, on the contrary, the yellow fluid be long exposed to a low temperature, sulphur crystallizes from it, and the decanted fluid allows the distillation of a much larger quantity without decomposition. In this distillation, again, chloride of amyle passes over with a yellow colour below 230° F. The authors could not detect chloride of thionyle in the first distillate.

When the distillation is continued, a very small quantity of a yellow fluid passes below 320° F., followed between 320° and 446° F. by a yellow distillate containing chlorine, which, when agitated with water, evolves sulphurous acid, deposits sulphur and amylic alcohol, and furnishes a solution of muriatic and hyposulphurous acids.—Liebig's *Annalen*, cix. p. 1.

Note on the Action of the Iodides of Methyle, Æthyle, and Amyle upon some Cyanides. *By* M. Schlagdenhauffen.

From observing the facility with which chloride of mercury is decomposed in presence of the above iodides, the author was led to try to obtain analogous reactions with the alkaline and metallic cyanides.

A solution of cyanide of potassium left to evaporate spontaneously in presence of an alcoholic solution of iodide of methyle or æthyle is not decomposed; these hydriodic æthers evaporate rapidly in consequence of their great volatility, and the remaining liquid con-

tains no iodide of potassium, showing that under these circumstances no decomposition takes place. By boiling these æthers with an alcoholic solution of cyanide of potassium, and returning the products of distillation several times, the cyanide is not decomposed. But when dry cyanide of potassium, mixed with alcohol and hydriodic, æthylic or methylic æther, is sealed in a tube and heated in the water-bath to 212° F., the interior of the tube is clotted with colourless cubical crystals in about half an hour. On opening the tube there is no evolution of gas; and on submitting the liquid contents of the tube to distillation, the formation of hydrocyanic æther, or of methylhydrocyanic æther, is recognized by the alliaceous odour. This liquid, treated in either case with potash and mixed with a sesquisalt of iron, gives origin to an abundant precipitate of prussian blue, which persists in presence of an excess of muriatic acid.

The decomposition of cyanide of potassium in presence of iodide of amyle takes place at a temperature rather higher than in the preceding cases. When the sealed tube is plunged into a chloride-of-calcium-bath at 284° F., the formation of large colourless cubical crystals is observed in the interior of the tube. The tube, when cooled and opened, emits an odour of cyanide of amyle; the distilled liquid, treated with caustic potash in presence of a sesquisalt of iron, furnishes prussian blue.

Cyanide of barium under similar circumstances, furnishes iodide of barium and the hydrocyanic æthers.

With cyanide of zinc the decomposition was not effected in six hours, although the tube containing the mixture was kept at a temperature between 284° and 320° F.

Other insoluble metallic cyanides could, however, be decomposed. Cyanide of silver, heated to 320° F. in the oil-bath with iodide of æthyle, was decomposed in two hours. Cyanide of æthyle and iodide of silver were formed. Iodide of lead and cyanide of æthyle were also obtained by submitting a mixture of 3·8 grms. of dry cyanide of lead and 4·6 grms. of iodide of æthyle to a temperature of 356° F. under pressure. The iodide of lead was crystalline and of a fine yellow colour, analogous to that obtained by boiling the amorphous iodide in water.—*Comptes Rendus*, January 24, 1859.

On Compounds of Boron. *By* C. A. Martius.

At the suggestion of Wöhler and Deville, the author has studied the behaviour of perchloride of boron to other bodies.

Chloride of Boron and Cyanogen, $BCl^3 + NC^2Cl$, is obtained when dry gaseous chloride of cyanogen is conducted into fluid chloride of boron. The gas is absorbed with a strong evolution of heat, and the chloride of boron is converted into a white, light, crystalline substance. When the chloride of boron is saturated even in the smallest proportion with chloride of cyanogen, the compound separates in colourless prisms.

This body has an odour of chloride of cyanogen, fumes slightly in moist air, and is converted by water into gaseous chloride of

cyanogen, boracic acid, and muriatic acid, with a violent evolution of heat. It behaves in the same way to absolute alcohol. At a pretty high temperature it is volatile with partial decomposition, leaving a white substance.

The analysis gave 61·3 per cent. of chlorine combined with boron, and 18·3 per cent. combined with cyanogen; a distinct determination of the total amount gave 79·7 per cent. of chlorine; these values lead to the above formula.

Perchloride of Boron and Ammonia, $2BCl^3 + 3NH^3$.—This compound was already prepared by Berzelius. The author obtained it by conducting dry ammonia into well-cooled chloride of boron. The combination takes place with a very violent evolution of heat.

It is a fine crystalline powder which does not fume in the air, but is decomposed by contact with water into muriate of ammonia, boracic acid, and muriatic acid. It sublimes without alteration. When driven with gaseous ammonia through a red-hot tube, it is converted into nitruret of boron. It contains 74·33 and 74·49 per cent. of chlorine.

Perchloride of Boron and Hydrocyanogen.—If the vapour of anhydrous hydrocyanic acid be conducted into refrigerated chloride of boron, a solid compound is obtained. This, however, is soon decomposed at the ordinary temperature into a brown fluid mass, so that it could not be further investigated.

Boride of Platinum.—That platinum and boron fuse together has already been discovered by Descotils, who states that boracic acid and charcoal, when heated with platinum in the blast-furnace, produce boride of platinum, which when dissolved furnishes boracic acid. Deville and Wöhler have found that boron, when heated before the blowpipe on platinum foil, immediately perforates it with formation of readily fusible, silver-white boride of platinum. The same alloy was obtained by Wöhler and Deville by fusing a mixture of spongy platinum and amorphous boron under a covering of borax. This alloy was fused into a single mass by placing it with a further addition of boron and borax in a charcoal crucible, and heating it in a strong coke fire. It was well fused, had the colour of platinum, and exhibited a distinct step-like cubical crystallization in a cavity. Its spec. grav. was 17·32. It split up with a single blow, and exhibited a laminar crystalline fracture. The author analysed a fragment of this boride of platinum; it was so brittle that it could easily be reduced to a fine powder. This was dissolved in nitromuriatic acid, which took place very slowly. A quantity of boracic acid separated from the solution.

Analysis gave 91·8 per cent. of platinum, according to which the alloy approaches the formula Pt^2B.—Liebig's *Annalen*, cix. p. 79.

On a New Mode of Production of the Alcoholic Alkalies.

By E. Juncadella.

The action of ammonia upon the compound æthers gives origin to two fundamental transformations which are essentially distinct;

sometimes the æther reproduces the generative alcohol, and the ammonia remaining, combined with the elements of the acid, constitutes a corresponding amide; sometimes the æther reproduces the acid itself, and the ammonia remains combined with the elements of the alcohol, forming an alcoholic amide endowed with alkaline properties; the former phænomenon is usually manifested with the æthers formed by the organic oxyacids, the second with those formed by the true hydracids.

The only æthers of a mineral oxyacid which have been examined in this point of view, are those of sulphuric acid; these furnished alcoholic alkalies. The author has investigated the nitric æthers of æthylic and methylic alcohols.

1. *Æthylonitric æther.*—This body was dissolved in four times its weight of absolute alcohol, the liquid saturated with dry gaseous ammonia, and then exposed to a temperature of 212° F., in hermetically sealed vessels; 15 or 16 hours are required for the decomposition; a great quantity of æthylamine was produced, and the author prepared and purified the hydrochlorate of this alkali by the usual methods. The analysis of the platinum double salt furnished—

	Found.	Calculated. ($C^4 H^7 N, HCl, PtCl^2$).
C	9·6	9·6
H	3·2	3·2
Pt	39·3	39·4

The formation of æthylamine in this case may be represented by the following equation:—

$$C^4 H^5 O, NO^5 + NH^3 = C^4 H^7 N, HO, NO^5.$$

Aqueous ammonia at 212° F., alcohol ammonia, and dry ammoniacal gas at the ordinary temperature, all act upon nitric æther and form æthylamine, although in but small quantity.

2. *Methylonitric æther.*—The decomposition of this by ammonia is far more easy than that of the preceding æther. The analysis of the platinum salt gave—

	Found.	Calculated. ($C^2 H^5 N, HCl, PtCl^2$).
C	5·1	5·1
H	2·8	2·5
Pt	41·5	41·7

The formation of methylamine under these circumstances is represented by the equation

$$C^2 H^3 O, NO^5 + NH^3 = C^2 H^5 N, HO, NO^5.$$

3. The formation of æthylamine and methylamine in the preceding conditions is so abundant that this reaction might be made use of for the preparation of these alkalies. For this purpose methylo- or æthylo-nitric æther is mixed with two or three times its weight of alcohol saturated with dry ammoniacal gas, the whole is placed in a thick glass tube so as to fill only the half of it; the tube is then sealed up and heated in the water-bath for two days, when it is removed and its contents distilled with an excess of

caustic potash, receiving the alkaline vapours evolved in dilute muriatic acid; the fluid obtained is evaporated to dryness, the mass is treated with ordinary alcohol, filtered, and again evaporated to dryness; and this mixture, consisting principally of hydrochlorate of methylamine or æthylamine, is treated with three times its volume of absolute alcohol, in which hydrochlorate of ammonia is very sparingly soluble; by evaporating this alcoholic solution the hydrochlorate of the alcoholic alkali is obtained tolerably pure.—*Comptes Rendus*, February 14, 1859, p. 342.

PROCEEDINGS OF SOCIETIES.

Royal Society.

Jan. 6, 1859.—Sir Benjamin C. Brodie, Bart., President, in the Chair.

"Contributions towards the History of the Monamines." By A. W. Hofmann, LL.D., F.R.S.

2. *Action of Bisulphide of Carbon upon Amylamine.*

In a note on the alleged transformation of thialdine into leucine, addressed to the Royal Society about eighteen months ago*, I alluded to a crystalline substance observed by Wagner when submitting amylamine to the action of bisulphide of carbon. This substance was not analysed, but considering its mode of formation, Wagner suggested that it might possibly be thialdine.

$$\underbrace{C_{10}H_{13}N}_{\text{Amylamine.}} + C_2S_4 = \underbrace{C_{12}H_{13}NS_4}_{\text{Thialdine.}}.$$

A superficial comparison of the properties of thialdine with those of the substance produced by the action of bisulphide of carbon upon amylamine, enabled me at once to recognize the difference of the two bodies; and satisfied with the result, I did not at the time examine more minutely into the nature of the latter substance.

The new interest conferred upon leucine by recent researches which characterize this substance as capronamic acid, has called my attention back to the sulphuretted derivative of amylamine.

This body may be readily procured by mixing anhydrous amylamine with a solution of dry bisulphide of carbon in anhydrous ether. The mixture becomes hot, and deposits, on cooling, white shiny scales which are scarcely soluble in ether, and may therefore be purified by washing with this liquid.

The new body is likewise insoluble in water, but readily dissolves in alcohol; when dry, it may be exposed for a time to a temperature of 100° C. without undergoing fusion; after some time, however, the substance begins to be liquefied and to undergo complete decomposition. The same change occurs, although more slowly, at the common temperature, when sulphuretted hydrogen is evolved; a mixture of free sulphur with a new crystalline substance, extremely fusible, insoluble in water, but soluble both in alcohol and ether, remaining behind.

* Chem. Gaz., Aug. 1, 1857, p. 298.

Analysis has proved that the compound produced by the action of bisulphide of carbon upon amylamine contains

$$C_{11}H_{13}NS_2, \text{ or rather } C_{22}H_{26}N_2S_4;$$

and that it is formed by the union of 2 equivalents of amylamine with bisulphide of carbon.

$$\underbrace{2C_{10}H_{13}N}_{\text{Amylamine.}} + C_2S_4 = \underbrace{C_{22}H_{26}N_2S_4}_{\text{New compound.}}$$

A glance at this formula suffices to characterize this compound as amylsulphocarbamate of amylamine.

$$C_{22}H_{26}N_2S_4 = C_{10}H_{13}N, C_{12}H_{13}NS_4 = \left.\begin{matrix}\left[(C_2S_2)''(C_{10}H_{11})HN\right] \\ \left[(C_{10}H_{11})H_2N\right]\end{matrix}\right\} S_2.$$

This view is easily confirmed by experiment. Addition of hydrochloric acid to the crystalline compound immediately separates an oily liquid, which gradually solidifies, and the acid solution now contains amylamine which may be liberated by potassa. The oily substance is obviously amylsulphocarbamic acid: it dissolves in ammonia and in potassa; mixed with amylamine, it reproduces the original crystalline compound.

Experiments with ethylamine have furnished perfectly analogous results. I have been satisfied to establish qualitatively the analogy of the reactions.

It is of some interest to compare the deportment of amylamine under the influence of bisulphide of carbon with that of phenylamine in the same conditions. If both bodies gave rise to similar changes, we should expect in the case of phenylamine the formation of phenylsulphocarbamate of phenylamine. But experiment has proved that phenylamine immediately produces diphenyl-sulphocarbamide (sulphocarbanilide), sulphuretted hydrogen being evolved—

$$\underbrace{2(C_{12}H_7N)}_{\text{Phenylamine.}} + C_2S_4 = \underbrace{C_{25}H_{12}N_2S_2}_{\text{Diphenylsulpho-carbamide.}} + H_2S_2.$$

Nevertheless it is extremely probable that further experiments will establish a perfect analogy in the deportment of bisulphide of carbon with amylamine and phenylamine. Diphenyl-sulphocarbamide is probably the product of decomposition of a very unstable phenylsulphocarbamate of phenylamine—

$$\underbrace{C_{25}H_{14}N_2S_4}_{\substack{\text{Phenylsulpho-carbamate of phenylamine?}}} = H_2S_2 + \underbrace{C_{25}H_{12}N_2S_2}_{\substack{\text{Diphenylsulpho-carbamide.}}},$$

while a more minute examination of the crystalline substance obtained by the action of heat upon amylsulphocarbamate of amylamine cannot fail to characterize it as diamylsulphocarbamide—

$$\underbrace{C_{22}H_{26}N_2S_4}_{\substack{\text{Amylsulphocarbi-mate of amylamine.}}} = H_2S_2 + \underbrace{C_{22}H_{24}N_2S_2}_{\substack{\text{Diamylsulpho-carbamide.}}}?$$

The apparent dissimilarity of the two reactions would thus be reduced to the unequal stability of the sulphocarbamic acids of the amyle- and phenyle-series.

"On New Nitrogenous Derivatives of the Phenyle- and Benzoyle-series." By P. Griess, Esq.

Piria's important discovery that the action of nitrous acid upon asparagine gives rise to the formation of malic acid, has led to a very general application of this agent in the study of nitrogenous substances. The results obtained have been almost always analogous to those produced by Piria; the reaction may be illustrated by the following examples:—

$$\underbrace{\left.\begin{matrix}(C_8H_4O_6)''\\H_4\end{matrix}\right\}}_{\text{Asparagine.}} N + 2NO_3 = H_2O_2 + 4N + \underbrace{\left.\begin{matrix}(C_8H_4O_6)''\\H_2\end{matrix}\right\}}_{\text{Malic acid.}} O_4.$$

$$\underbrace{\left.\begin{matrix}C_{12}H_5\\H_2\end{matrix}\right\}}_{\text{Phenylamine.}} N + NO_3 = HO + 2N + \underbrace{\left.\begin{matrix}C_{12}H_5\\H\end{matrix}\right\}}_{\text{Phenol.}} O_2.$$

The plan hitherto adopted consisted in submitting the *aqueous* solution of the nitrogenous body directly to the action of nitrous acid, or in dissolving the body in nitric acid, and passing into the solution a current of binoxide of nitrogen. By employing *alcoholic* and *ethereal* solutions, I have arrived at different results, establishing a *new mode of reaction*; of the facts which I have observed the following may be quoted as illustrations.

Action of Nitrous Acid on Picramic Acid. Diazodinitrophenol.

On passing a current of nitrous acid into an alcoholic solution of picramic acid—

$$C_{12}H_5N_3O_{10} = C_{12}\left(\begin{matrix}H_3\\(NO_4)_2\\H_2N\end{matrix}\right)O_2,$$

the red liquid assumes at once a yellow colour, and furnishes rapidly a copious deposit of yellow crystals. *No gas is evolved during the reaction.* The yellow crystals, purified by recrystallization from alcohol, are found to contain

$$C_{12}H_2N_4O_{10},$$

and are obviously formed according to the equation—

$$C_{12}H_5N_3O_{10} + NO_3 = 3HO + C_{12}H_2N_4O_{10}.$$

The new body, for which I propose the provisional name *diazodinitrophenol*, is soluble in alcohol and ether, and crystallizes from the former solvent in magnificent golden-yellow plates, which detonate on heating. Acids have no action upon this substance; on ebullition with water it appears to undergo decomposition; alkalies induce at once a copious evolution of gas, and give rise to the formation of dinitrophenol. This metamorphosis appears to indicate that the new body still belongs directly to the phenol-group; the constitu-

tion of diazodinitrophenol may perhaps be best understood by representing it by the formula

$$C_{12}\left(\begin{matrix}H_2\\(NO_4)_2\\N_2\end{matrix}\right)O_2.$$

The transformation of this compound into

$$C_{12}\left(\begin{matrix}H_4\\(NO_4)_2\end{matrix}\right)O_2$$

involves the decomposition of 2 equivs. of water, the oxygen of which appears to be consumed in the formation of secondary products of decomposition. No trace of oxygen, either free or combined, could be found among the gaseous products; the gas evolved consisting, according to a minute examination, of perfectly pure nitrogen.

Diazonitrochlorphenol.

Treatment in a similar manner of *amidonitrochlorphenol*

$$C_{12}H_4ClNO_6=C_{12}\left(\begin{matrix}H_2\\Cl\\NO_4\\H_2N\end{matrix}\right)O_2,$$

a new mixed derivative of phenol, as might have been expected, has furnished perfectly similar results. The new compound thus obtained crystallizes in beautiful brown-red needles, of physical and chemical properties similar to those of the preceding compound. It contains

$$C_{12}H_2ClN_3O_6=C_{12}\left(\begin{matrix}H_2\\Cl\\NO_4\\N_2\end{matrix}\right)O_2.$$

Diazonitrophenol.

This substance is formed by submitting the ethereal solution of *diphenamic acid*,

$$C_{24}H_{12}N_4O_{12}=C_{24}\left(\begin{matrix}H_8\\(NO_4)_2\\(H_2N)_2\end{matrix}\right)O_2,$$

discovered by Gerhardt and Laurent, to the action of nitrous acid. It is a yellow, crystalline, very unstable compound, containing

$$C_{24}H_6N_6O_{12}=C_{24}\left(\begin{matrix}H_6\\(NO_4)_2\\N_4\end{matrix}\right)O_4;$$

it explodes with extreme violence at the temperature of boiling water. The alkalies decompose it instantaneously with evolution of nitrogen and formation of products which are not yet analysed.

Action of Nitrous Acid upon Benzamic Acid.

The product obtained in a similar manner from *benzamic acid* is an orange-yellow crystalline precipitate, which constitutes a dibasic

acid of the formula

$$C_{24}H_{11}N_3O_8.$$

Its formation is illustrated by the following equation:

$$\underbrace{C_{24}H_{14}N_2O_8}_{\text{2 equivs. of benzamic acid.}}+NO_3=3HO+\underbrace{C_{24}H_{11}N_3O_8}_{\text{New acid.}}.$$

This acid is insoluble in water, alcohol, and ether. It is dissolved without decomposition by the alkalies in the cold, giving rise to the formation of soluble crystalline salts, which produce precipitates with nitrate of silver and acetate of lead.

All these salts are decomposed on heating, with evolution of nitrogen gas. The action of fuming nitric acid upon the dibasic derivative of benzamic acid produces a new acid, furnishing with barium a splendid yellow crystalline salt. The dibasic acid is likewise decomposed by hydrochloric acid; in combination with this acid remains a body which can be sublimed in white crystals.

An alcoholic solution of benzamic ether when treated with nitrous acid yields the ether of the acid previously described.

The action of nitrous acid on alcoholic solutions of cuminamic and anisamic acids has likewise furnished new bodies, with the study of which I am at present engaged.

Action of Nitrous Acid on Phenylamine and Nitrophenylamine.

Phenylamine, when submitted to the modified nitrous acid-process, is transformed into a fusible body containing

$$C_{24}H_{11}N_3,$$

which is insoluble in water and easily soluble in alcohol. This compound, which possesses feebly basic characters, is formed according to the equation

$$\underbrace{C_{24}H_{14}N_2}_{\text{2 equivs. of Phenylamine.}}+NO_3=3HO+\underbrace{C_{24}H_{11}N_3}_{\text{New compound.}}.$$

Nitrophenylamine (the alpha-variety which is formed by the action of reducing agents upon dinitrobenzol), similarly treated, furnishes a compound crystallizing in beautifully red needles,

$$C_{24}H_9N_5O_8,$$

the formation of which is represented by the equation

$$\underbrace{C_{24}H_{12}N_4O_8}_{\text{2 equivs. of Nitrophenylamine.}}+NO_3=3HO+\underbrace{C_{24}H_9N_5O_8}_{\text{New compound.}}.$$

Treated with concentrated hydrochloric acid, the new compound reproduces nitrophenylamine. The action of chlorine and bromine upon it gives rise to the formation of new crystallized derivatives.

THE CHEMICAL GAZETTE.

No. CCCXCIX.—June 1, 1859.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On a Yellow Colouring Matter obtained from the Leaves of the Polygonum Fagopyrum, *or Common Buckwheat. By* Edward Schunck, Ph.D., F.R.S.

Among the many plants which have been supposed to contain or yield indigo-blue, the *Polygonum Fagopyrum* or common buckwheat, a plant extensively cultivated in some countries for the sake of its seed, which is used as an article of food, is mentioned by some authors. In the 'Mechanics' Magazine' for November 1830, for instance, the following directions are given for obtaining a blue colour from this plant:—"Take the buckwheat out of the ground before the seed has become quite hard, and lay it on the ground in the sun until it is dry. Then throw the plant into heaps, moisten it and allow it to ferment until decomposition commences, when it will assume a blue colour. It must now be formed into cakes, which may be dried either in the sun or in a stove. It imparts to boiling water a blue colour, which is not changed either by acetic or sulphuric acid. A durable blue may be dyed with it." Though it does not follow from this that the blue colouring matter thus obtained was really indigo-blue, still it seemed not improbable that it might be identical with the latter, since another species belonging to the same genus, the *Polygonum tinctorium*, is remarkable for the large amount of indigo-blue which it affords. Nevertheless, on submitting the leaves of the plant to the same process as that previously employed in the case of the *Isatis tinctoria* and other plants producing indigo, I was unable to obtain a trace of that or any other blue colouring matter. The examination led, however, to the discovery of a crystallized yellow colouring matter, the method of preparation and properties of which I shall now proceed to describe.

The plant, which is one easily cultivated and will grow in the poorest soils, having been allowed to attain its full size, the leaves

are separated from the stalks, and treated for some time with boiling water. The decoction, which is muddy and of a greenish colour, is strained through calico, and the mass remaining behind is well pressed, in order to remove all the liquid. A little acetate of lead is now added to it. This produces a bulky yellowish-green precipitate, consisting of chlorophyll and other impurities in combination with oxide of lead. Care must be taken to add only so much acetate of lead as to render the supernatant liquid clear and transparent, as an excess would precipitate a portion of the colouring matter. The liquid, having been again raised to the boiling-point, is filtered boiling. It has a fine golden-yellow colour, but on being mixed with a quantity of acetic acid it becomes pale yellow, and on being now allowed to stand for some time it deposits a voluminous mass of small yellow crystalline needles. These are collected on a filter, slightly washed with cold water, and then redissolved in boiling water, to which a little acetic acid is added. A small quantity of white matter is usually left undissolved, which is separated by filtration. The filtered liquid again deposits, on cooling and standing, a mass of crystals, which, after being collected on a filter and washed with cold water, are dissolved in boiling alcohol. The alcoholic solution is filtered from a small quantity of insoluble matter, and then distilled until the greatest part of the spirit has passed over. The dark yellow liquid left in the retort is then poured into a dish, and allowed to stand for some time, when it deposits the pure colouring matter as a mass of crystalline needles of a pale primrose-yellow colour. These are collected on a filter, washed with a little cold alcohol, and allowed to dry spontaneously. Its properties are as follows :—

It is perfectly tasteless, and its solutions are neutral to test-paper. When heated on platinum foil it melts to a brown transparent liquid, and then burns with a yellow flame, leaving much charcoal, which, on being heated, burns slowly away without leaving any ash. When heated in a tube it melts, gives off fumes having a strong empyreumatic smell, and yields a yellow oily sublimate, in which nothing crystalline is formed even after several days. It is hardly soluble in cold water, and only sparingly soluble in boiling water. The boiling watery solution deposits it on cooling in yellow silky needles, which, when dry, form a compact silky mass. It is more easily soluble in boiling alcohol than in water. It does not separate from the alcoholic solution on cooling, but is left on evaporation in star-shaped masses of a darker yellow colour than the needles obtained from the watery solution. Strong muriatic acid changes its colour to a deep yellow without decomposing it. When concentrated sulphuric acid is brought into contact with it, the acid acquires at first a greenish colour, and then dissolves it entirely, forming a deep yellow solution, from which the greatest part of the colouring matter is precipitated by water in yellow flocks. If, however, the solution in acid be heated, it becomes black and gives off sulphurous acid in abundance, the colouring matter being decomposed. When the substance is dissolved in boiling water to which a little

sulphuric acid has been added, and the solution is boiled for some time, no decomposition apparently takes place, proving that this colouring matter is not, like some others, a copulated compound. Nitric acid of ordinary strength dissolves it even in the cold, forming a dark orange-coloured liquid, which, on being boiled, evolves nitrous acid, and becomes pale yellow; the liquid on evaporation yielding a large quantity of oxalic acid. When suspended in water, and exposed to the action of chlorine gas, it gradually dissolves, forming a brownish-yellow solution, which on evaporation leaves a brownish-yellow glutinous residue. This residue has an astringent taste, which is, however, partly disguised by the muriatic acid formed during the decomposition; its watery solution gives with gelatine a curdy precipitate, similar to that produced with the latter by tannin. The colouring matter dissolves easily in caustic potash and soda, liquid ammonia, baryta-water and lime-water, forming deep yellow solutions, which, on the addition of an excess of acid, become pale yellow, and on standing again deposit the colouring matter in pale yellow needles. If, however, these solutions be left to stand for some time exposed to the air, a decomposition of the colouring matter seems to take place, for on now adding an excess of acid, the solutions remain yellow, and deposit no crystals. If the ammoniacal solution be left exposed to the atmosphere for some time and then evaporated, it leaves a residue consisting of crystals of colouring matter mixed with an amorphous substance. On adding water to the residue the latter dissolves, and the solution, after being filtered from the crystals and evaporated, leaves a transparent, yellow, brittle mass resembling gum, which contains only a trace of ammonia, and is probably a product of decomposition formed by the action of the atmospheric oxygen on the colouring matter.

The watery solution produces, with different reagents, the following reactions. With acetate of alumina it gives a bright yellow flocculent precipitate; the filtered liquid is still very yellow, but on the addition of ammonia it deposits some more yellow precipitate, and then appears colourless. With protosulphate of iron it turns of a greenish colour, but on standing exposed to the air the colour changes to a dark green, whilst a dark green powder is deposited; the addition of ammonia now produces a dark brown precipitate, the liquid becoming colourless. On the addition of perchloride of iron it turns of a brownish-olive colour. Both the watery and the alcoholic solution give with acetate of lead a precipitate of a bright yellow colour, inclining to orange, which very much resembles that of chromate of lead; the filtered liquid in either case still retains some of its yellow colour. With basic acetate of lead the watery solution gives a precipitate of a rather darker yellow colour than that with neutral acetate, the filtered liquid being colourless. The watery solution when cold becomes on the addition of acetate of copper greenish yellow, and remains clear, but on being boiled it deposits an abundant greenish-yellow precipitate, which dissolves again almost entirely when the liquid cools. The

watery solution gives no precipitate with nitrate of silver, but on standing it becomes muddy and black, and deposits a fine black powder. On the addition of chloride of gold it also soon becomes muddy, and deposits bright spangles of metallic gold; when caustic soda is added at the same time, the reduction takes place instantaneously, the gold being deposited partly as a black powder, partly as a metallic mirror covering the sides of the glass. Protochloride of tin produces in the watery solution a bright yellow precipitate, the supernatant liquid remaining muddy for a long time.

Printed calico, when immersed in the warm watery solution of this colouring matter, becomes fully dyed, the alumina mordant acquiring a dark yellow colour, the tin mordant a light yellow, and the iron mordant various shades of yellowish brown, according to the strength of the mordant employed. Silk and wool do not acquire any colour in the boiling watery solution, unless they have been previously prepared with some mordant.

The substance contains no nitrogen, for on being treated with boiling caustic soda-lye, or heated in a tube with soda-lime, it evolves no ammonia. Composition in 100 parts—

	I.	II.	III.	IV.
Carbon	49·67	49·73	50·03	49·96
Hydrogen	5·89	5·79	5·95	5·92
Oxygen	44·44	44·48	44·02	44·12

The lead compound was prepared by adding to the alcoholic solution an alcoholic solution of acetate of lead. The dark yellow precipitate was collected on a filter, washed with cold alcohol, and dried over sulphuric acid. It yielded on being analysed the following results:—

0·9555 grm. gave 1·1315 grm. carbonic acid, and 0·3090 water.
0·7630 grm. gave 0·4025 grm. sulphate of lead.

From these numbers may be deduced the following composition:—

	Equivs.		Calculated.	Found.
Carbon	30	180	31·83	32·29
Hydrogen	18	18	3·18	3·59
Oxygen	18	144	25·48	25·31
Oxide of lead	2	223·4	39·51	38·81

If the formula of the lead compound is $C^{30}H^{18}O^{18}+2PbO$, as the above analysis seems to indicate, then that of the substance in its uncombined state must be $C^{30}H^{20}O^{20}$, and its theoretical composition will be as follows:—

	Equivs.		
Carbon	30	180	50·00
Hydrogen	20	20	5·55
Oxygen	20	160	44·45

A comparison of the properties and composition of this substance with those of *Rutine* or *Rutic Acid*, the colouring matter

discovered by Weiss* in the *Ruta graveolens* or common rue, and by Rochleder and Hlasiwetz† in capers, leads to the conclusion that they are identical. A colouring matter, having the same properties and composition, and being apparently the same substance, has also lately been discovered by Moldenhauer‡ in the leaves of the *Ilex aquifolium* or common holly, and called by him *Ilixanthine*. The quantity to be obtained from the buckwheat leaves seems, however, to be much more considerable than that procurable from any other source. In one experiment I found that 30lbs. of fresh leaves yielded 240 grains of crystallized rutine, or a little more than the thousandth part of their weight. In countries where the plant is cultivated it might be worth while to collect the leaves as a dyeing material, since the seeds are the only part at present employed for any useful purpose.—From the *Memoirs of the Literary and Philosophical Society of Manchester*, 1858.

Compounds of Alloxan with Alkaline Bisulphites. *By* Dr. Wuth.

The composition of the three compounds that may be prepared from uric acid, alloxantine, purpuric acid, and thionuric acid, may be represented as follows:—

$$\underset{\text{Alloxantine.}}{C^{16}H^4N^4O^{14}} = \underset{\text{Dialuric acid.}}{C^8H^4N^2O^8} + \underset{\text{Alloxan.}}{C^8H^2N^2O^8} - 2HO$$

$$\underset{\text{Purpuric acid.}}{C^{16}H^5N^5O^{12}} = \underset{\text{Dialuramide.}}{C^8H^5N^3O^6} + \underset{\text{Alloxan.}}{C^8H^2N^2O^8} - 2HO$$

$$\underset{\text{Thionuric acid.}}{C^8H^5N^3S^2O^{12}} = \underset{\text{Dialuramide.}}{C^8H^5N^3O^6} + \underset{\text{Sulphuric acid.}}{S^2H^2O^8} - 2HO$$

From this it appears probable that a fourth compound, $C^8H^4N^2S^2O^{14}$, may be prepared, standing in the same relation to thionuric acid as alloxantine to purpuric acid. Its composition would therefore be

$$\underset{\text{New compound.}}{C^8H^4N^2S^2O^{14}} = \underset{\text{Dialuric acid.}}{C^8H^4N^2O^8} + \underset{\text{Sulphuric acid.}}{S^2H^2O^8} - 2HO$$

In experiments with the view of preparing this body, which might be an acid, the author caused alkaline bisulphites to act upon alloxan; he did not, however, obtain that body, but found that the salts combined directly with alloxan, so that the behaviour of alloxan may be compared with that of aldehyde.

Alloxan with Bisulphite of Potash, $C^8H^3KN^2S^2O^{14} + 2HO$.—Powdered alloxan is added to a concentrated solution of bisulphite of potash, with constant stirring assisted by a gentle heat, as long as it is dissolved; the filtered fluid, after standing for some hours, deposits large, well-developed crystals of the new compound, which dissolve with some difficulty in cold, but with ease in hot water, and

* Pharmaceut. Centralblatt, 1842, p. 903.
† Chem. Gaz. vol. x. p. 254.
‡ Chem. Gaz. vol. xv. p. 304.

have a slightly acid reaction. At 212° F. they lose their water of crystallization, and acquire a slight red colour. Analysis:—

C	17·1		8=48		17·1
H	2·3		5	5	1·8
K	14·5	13·6	1	39	13·9
N			2	28	
S^2O^4	23·1	23·3	1	64	22·8
O			12	96	
Water of crystallization	6·4				6·4

Alloxan with Bisulphite of Soda, $C^8H^3NaN^2S^2O^{14}+3HO$.—Prepared like the potash compound; it forms large crystals which are far more soluble than those of the preceding. The water of crystallization escapes at 212° F. with slight reddening of the residue. Analysis:—

C	18·1	8=	48	17·6
H	2·7	6	6	2·2
Na	8·5	1	23	8·4
N		2	28	
S^2O^4	22·9	1	64	23·4
O		13	104	
Water of crystallization	9·7			9·8

Alloxan with Bisulphite of Ammonia, $C^8H^3(NH^4)N^2S^2O^{14}+2HO$.—Alloxan is dissolved by bisulphite of ammonia. The compound resembles the two preceding, but is far more soluble in water. Analysis:—

C	18·7	18·4	8	48=	18·5
H	3·6	3·7	9	9	3·4
N	15·5		3	42	16·2
S^2O^4	24·3		1	64	24·7
O			12	96	
Water of crystallization	7·1				6·9

The above-described potash-salt appears, as the author remarks, to have been previously observed by Gregory.

Alloxantine does not appear to form compounds of this kind. If a hot saturated solution of alloxantine be mixed with bisulphite of ammonia, crystals of dialurate of ammonia are deposited on cooling.—Lebig's *Annalen*, cviii. p. 41.

On the Conversion of Lactic Acid into Propionic Acid.
By Dr. C. Ulrich.

The following experiments were made for the purpose of submitting to the test of experiment the supposition that the compound $C^6H^4O^2Cl^2$, recently prepared by Wurtz from lactic acid and termed by him chlorolactyle, was the chloride of chloropropioxyle

$$\left(C^4\left\{\begin{matrix}H^4\\Cl\end{matrix}\right)C^2O^2, Cl.\right.$$

If this view were correct, we should expect that the supposed

chloride would decompose with water into chloropropionic acid and muriatic acid, and that the product of the action of alcohol on the compound described by Wurtz as chlorolactic æther would be the chloropropionate of the oxide of æthyle

$$\left(C^4\left\{\begin{matrix}H^4\\Cl\end{matrix}\right)C^2O^2, Cl + 2HO = HO\,.\left(C^4\left\{\begin{matrix}H^4\\Cl\end{matrix}\right)C^2O^2, O + HCl.\right.\right.$$

Chloride of chloropropioxyle. Chloropropionic acid.

$$\left(C^4\left\{\begin{matrix}H^4\\Cl\end{matrix}\right)C^2O^2, Cl + C^4H^5O\,.\,HO = C^4H^5O\,.\left(C^4\left\{\begin{matrix}H^4\\Cl\end{matrix}\right)C^2O^2, O + HCl.\right.\right.$$

Chloride of chloropropioxyle. Chloropropionic æther.

It is true that the statement of Wurtz, that he reproduced lactic acid from the so-called chlorolactyle by decomposition with water, is opposed to the resulting compound being chloropropionic acid. However, I repeated the experiment, and found, as I suspected, that lactic acid is only then produced when in the decomposition of the chlorolactyle by water an alkali or some strong base takes part in the action, but that when the decomposition is effected solely by water, no *lactic acid* is formed, but only *chloropropionic acid.*

The colourless fuming liquid (the mixture of chloride of chloropropioxyle and oxychloride of phosphorus) which is obtained by heating dry lactate of lime with pentachloride of phosphorus was gradually added in small portions to a large quantity of water, and the acid liquid, which contained much phosphoric and hydrochloric acid, distilled to about half its volume. The distillate contained chloropropionic acid and muriatic acid. The residue in the retort which should have contained the lactic acid, had any been formed, was further evaporated in the water-bath in order to remove the chloropropionic acid still contained in it as much as possible, and then tested for lactic acid. Not a trace of lactic acid could be found in it.

The acid distillate containing the chloropropionic acid was neutralized in the cold with freshly precipitated carbonate of silver, the filtered saline solution evaporated to dryness *in vacuo* over sulphuric acid, and the beautiful colourless prisms of chloropropionate of silver analysed. I convinced myself by a preliminary experiment, that on being heated, it gives off acid vapours and leaves a residue, which consists principally of chloride of silver, but also contains some metallic silver. A small quantity of the chloropropionic acid escapes undecomposed on heating the silver-salt, as is evident from the odour of the vapours. Analysis gave—

Carbon.....	16·5	6 =	36·0	16·7
Hydrogen ..	1·9	4	4·0	1·8
Chlorine	..	1	35·5	
Oxygen	..	4	32·0	
Silver	50·2	1	108·0	50·1

Chloropropionate of silver is far more soluble in water than the p ropionate; it is slightly blackened by exposure to light. On boiling

the aqueous solution, chloride of silver separates, and lactic acid is formed. The lead-salt experiences the same decomposition on evaporating its solution in the water-bath. The chloropropionic acid is far less volatile than the propionic acid, and possesses an odour resembling that of trichloracetic acid.

To obtain a further proof that the acid was really chloropropionic acid, I tried to convert it directly into propionic acid, and succeeded in the following manner:—The crude chloride of chloropropioxyle, still containing oxychloride of phosphorus, was allowed to flow gradually into a vessel containing water and a tolerable quantity of granulated zinc. The hydrogen, disengaged by the phosphoric and hydrochloric acids from the zinc and water, was to replace the chlorine in the generated chloropropionic acid. A copious evolution of gas immediately resulted; and when the oil drops and the smell of the chloride of chloropropioxyle and oxychloride of phosphorus had disappeared, the acid liquor poured from the zinc was further diluted with water, and submitted to distillation. The distillate contained a considerable quantity of pure propionic acid along with traces of hydrochloric acid. It was neutralized with carbonate of soda, evaporated to dryness, and distilled with dilute sulphuric acid. A portion of the strongly acid fluid which passed over, and which smelt distinctly of propionic acid, was boiled with carbonate of silver; on cooling, pure propionate of silver separated from the hot-filtered solution in beautiful crystals, which slowly became black by exposure to light. On analysis they furnished—

	Found.	Calculated according to AgO, $C^6 H^5 O^3$.
Carbon	19·6	19·9
Hydrogen	2·8	2·7
Oxygen	..	17·8
Silver	59·8	59·6

I also prepared the potash-salt which furnished 35·3 per cent. potassium; the formula $KO, C^6 H^5 O^3$ requires 34·8 per cent.

The above method of preparing propionic acid is so productive and furnishes such a pure acid that it probably deserves the preference.

I also attempted to prepare the propionic æther from the chloropropionic æther by treatment with zinc and dilute sulphuric acid, but it appears at the moment of its origin to be decomposed, probably by the free sulphuric acid present, into propionic acid and alcohol.—Liebig's *Annalen*, March 1859, p. 268.

On the Phosphide of Molybdenum. *By* Prof. Wöhler.

This compound was procured by the process recently described by the author, for the preparation of the crystallized phosphide of tungsten. 10 grms. of yellow molybdic acid, containing some phosphoric acid, and 20 grms. of fused phosphoric acid containing lime, were exposed in a carbon crucible for an hour to an intense

coke fire. The product was a vesicular gray metallic mass, the cavities of which were lined with minute crystals of a metallic lustre, which proved to be phosphide of molybdenum. The whole mass consisted of it, but intimately mixed with phosphate of lime, from which it was purified by alternate treatment with muriatic acid and solution of caustic soda.

Thus prepared, it forms a gray crystalline powder of 6·167 spec. grav. It is evidently very difficult of fusion. When heated to redness in the air, it gradually becomes oxidized without burning. Hot concentrated nitric acid slowly converts it into phosphoric and molybdic acids. Thrown upon fusing nitre, it is oxidized with incandescence. Heated gently in chlorine, it is converted into chloride of molybdenum and chloride of phosphorus. It is a conductor of electricity. In contact with zinc in muriatic acid it evolves hydrogen. On the addition of a salt of copper, copper is reduced on its surface.

The phosphide of molybdenum consists of $Mo^2 P$. For analysis, it was oxidized by being fused with a mixture of carbonate and nitrate of soda, the mass dissolved in water, the solution mixed with sulphide of ammonium, then warmed, and the sulphide of molybdenum precipitated with dilute nitric acid. When all the sulphuretted hydrogen had evaporated, it was collected on a dried weighed filter, washed, dried, and weighed. To remove the sulphur mixed with it and convert the sulphide into bisulphide, a weighed quantity was heated in hydrogen until no more sulphur was volatilized. The phosphoric acid contained in the liquid filtered from the sulphide of molybdenum, was precipitated in the usual way by chloride of magnesium and ammonia. The following numbers were obtained:—

		Found.	Calculated.
Molybdenum..	74·1	73·7	74·8
Phosphorus ..	24·9	..	25·2

Liebig's *Annalen*, March 1859.

Analysis of Highland "Cutweed" Kelp. *By* John Lamont, *Student in* Dr. Wallace's *Laboratory, Glasgow**.

Although kelp is prepared in large quantities for the iodine manufacture, very few analyses have been made of it. Indeed the only reliable analysis published in the chemical journals is that of a specimen of Orkney "drift-weed" by Mr. George W. Brown†.

The subject of the present analysis is cutweed kelp, so called from its being prepared from sea-weeds cut away from the rocks at low water. It was manufactured at the Island of Uist, one of the Hebrides, during the summer of 1858.

The method of analysis was similar to that adopted by Mr. Brown, with improved processes, however, for the estimation of the phosphoric acid, alumina, and iodine. The phosphoric acid existing

* Communicated by the Author.

† Proceedings of the Phil. Soc. of Glasgow, vol. iii. p. 208.

in the insoluble matter is calculated into phosphate of lime, but the precipitate obtained by the addition of ammonia contained a considerable quantity of magnesia, as well as alumina and oxide of iron. The iodine was estimated by the process described in the 'Chemical Gazette' for the present year, p. 137; the mean of three determinations was taken. The silicate of lime was calculated according to the formula $2CaO, SiO^3$.

The general analysis gave as follows:—

Soluble salts	60·9
Insoluble „	36·1
Moisture	3·0
	100

Soluble Salts.

Sulphate of potash	7·74
Chloride of potassium	19·86
Chloride of sodium	3·47
Iodide of sodium	·20
Sulphide of sodium	2·92
Hyposulphite of soda	1·98
Sulphite of soda	2·71
Sulphate of soda	15·10
Phosphate of soda	·95
Carbonate of soda	5·15
Loss	·82—60·9

Insoluble Salts.

Sulphide of calcium	2·09
Phosphate of lime	6·44
Carbonate of lime	11·17
Magnesia	5·70
Alumina	·23
Oxide of iron	1·42
Silicate of lime	2·77
Sand	1·65
Carbonaceous matter	3·30
Loss	1·33—36·1
Moisture	3·00
	100

The process adopted in the manufacture of kelp is well known to have two very serious objections, the volatilization of a portion of the iodine, and the reduction of a part of the sulphuric acid, giving rise to the presence of sulphides, hyposulphites, and sulphites in the product. The following process has been tried on the small scale with marked success. The weeds are boiled with a small quantity of water, the liquor evaporated to dryness, and the residue charred very carefully. The mass, dissolved in water, gives a colourless solution which is quite free from sulphides, and may be at once

boiled down to extract the salts, as in an iodine work, or simply evaporated to dryness, and sold as kelp. I am enabled, by the kindness of Dr. Wallace, to give an analysis of kelp so prepared, chiefly from *Laminaria digitata*.

Sulphate of potash	14·35
Chloride of potassium	42·49
Chloride of sodium	36·47
Sulphate of soda	3·90
Iodide of sodium	1·78
Carbonate of soda.....	1·01
	100

On Nitruret of Niobium. *By* H. Rose,

If ammoniacal gas be passed over niobic acid at a strong red heat, the latter is converted into nitruret of niobium, with formation of water. It is difficult, however, to decompose the whole of the acid in this way; the product obtained, which is a black powder, contains more or less niobic acid. Nevertheless it conducts electricity very well, but shows no metallic lustre. When fused with hydrate of potash, it evolves much ammoniacal gas, and on the entrance of air, it burns with brilliancy to form niobic acid.

When niobic acid is heated in a stream of gaseous cyanogen it is rapidly decomposed. The compound obtained is a deep black powder, which conducts electricity very well, but contains carbon as well as nitrogen, although in far smaller proportion than is necessary to form cyanogen with the nitrogen.

Nitruret of niobium is obtained in the purest state by heating perchloride of niobium in gaseous ammonia. Black crusts of nitruret of niobium are then produced with formation of muriate of ammonia; the latter may be entirely got rid of by treatment with water. It is a heavy, deep black powder, which is scarcely acted upon by nitric acid, or even by nitromuriatic acid, but is readily attacked by a mixture of nitric and hydrofluoric acid, when it evolves red fumes. *Bericht der Akad. der Wiss. zu Berlin*, 1859, p. 12.

ANALYTICAL CHEMISTRY.

On the Determination of Copper. *By* MM. Mathieu Plessy *and* Moreau.

This process depends on the known fact of the reduction of the salts of copper by copper itself under certain conditions. The sample to be analysed is dissolved in a mixture of pure fuming muriatic acid and chlorate of potash (8 cub. centims. of HCl and 1·200 gr. of $KO.ClO^5$ to 1 grm. of material). The reaction is effected in the cold, and when the action, which takes place at first rather tumultuously, slackens, the mixture is to be stirred; when stirring is not sufficient to continue the action, this is done by means

of a very gentle heat, carefully avoiding ebullition. When the solution is complete, 2 cub. centims. of sulphuric acid and 2 cub. centims. of water are introduced to each gramme of material, when the whole is boiled for five or six minutes, after which all the chlorate is decomposed, and the chlorine driven off. Muriate of ammonia is then added, and water immediately afterwards (about 6 grms. of NH^3 HCl and 20 cub. centims. of water). This salt dissolves; ammonia is added, but the liquid must retain a slight acidity, for which purpose it may be rendered slightly alkaline, and then treated with a few drops of muriatic acid.

The liquid is then rapidly boiled, and during the ebullition the reducing slip of copper twisted into a spiral form is introduced: this slip must be thin, and about three and a half times the weight of the sample. The liquid is immediately decolorized, passing from green to yellow, and from yellow to white. At this point, which is attained in 20 to 30 seconds, the liquid is decanted, the matrass is rinsed, then filled with water, and turned upside down over a crucible; in this way the reducing slip is withdrawn, and dried. The loss of weight of the slip indicates the weight of copper contained in the material examined.

The metals most usually associated with copper, such as zinc, lead, and tin, have no injurious effect upon the accuracy of the result. But this is not the case with iron. A plate of copper in fact causes a mixture of salts of copper to pass to a minimum, and of iron to a maximum.—*Comptes Rendus*, January 24, 1859, p. 240.

On the Recognition of Blood-spots. *By* M. Brücke.

The author publishes a test for blood which, according to him, furnishes perfectly accurate results with quantities of blood so small, that former methods could not be employed with them.

In 1853 Teichmann discovered that by the action of acetic acid upon blood crystals may be obtained, the essential constituent of which he afterwards found to be the colouring matter of the blood. From his own experiments, Brücke found Teichmann's statements perfectly correct, and that extremely small quantities of blood are sufficient to render this behaviour available for the detection of blood-spots in judicial cases—nay, that even when the blood-corpuscles are destroyed by attempts at cleaning, this does not prejudice the test, so long as any colouring matter has been left. The crystals are so characteristic, and produced under such circumstances, that any illusion is impossible. The course to be adopted is as follows:—

Some of the fluid obtained by extracting the spot with distilled water is put into a watch-glass, mixed with a few drops of solution of chloride of sodium, and left to dry under the air-pump with sulphuric acid. The watch-glass is then inspected with the microscope, to ascertain that nothing is there that could be confounded with Teichmann's crystals. The residue on the bottom of the watch-glass is then treated with glacial acetic acid, and evaporated

to dryness on the water-bath at 212° F.; a few drops of distilled water are poured into the watch-glass, and this is placed under the microscope to see whether any crystals have been formed. If there be too much substance at the bottom of the watch-glass to allow the examination to take place, portions may be spread upon glass slides covered with thin glass and then examined.—*Zeitschrift für Natur- und Heilkunde in Ungarn*, 1857; *Archiv der Pharm.* cxlvii. p. 71.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Manufacture of Sulphate of Baryta. By J. Pelouze.

Several manufacturers of chemicals prepare sulphate of baryta, known by the name of "*baryta-white*," by treating native carbonate of baryta with hydrochloric acid, and precipitating the solution obtained by sulphuric acid; thus regenerating the hydrochloric acid which may be used for further operations.

This sulphate, in spite of its being dearer than that which is prepared by other less costly processes, is always preferred to the latter for painting.

I have discovered that a sulphate of baryta, similar to that now in question, can be obtained by treating directly carbonate of baryta with dilute sulphuric acid, without its being necessary to pulverize the former. A very small quantity of hydrochloric acid, 3 to 4 hundredths for example, is added to the diluted sulphuric acid, and the whole kept at a slight ebullition. The pieces of carbonate of baryta, no matter how large, are acted upon and completely transformed into a fine white powder entirely composed of sulphate of baryta, and of the greatest tenuity.

If the same experiment is made without the addition of hydrochloric acid, the carbonate is acted upon very slowly. The part which hydrochloric acid plays in this reaction is easily understood. It forms a soluble chloride of barium which sulphuric acid decomposes, reproducing hydrochloric acid always in the same quantity, so that it is in fact the latter acid, not the sulphuric acid, which acts upon the carbonate of baryta.

This experiment becomes still more interesting if dilute sulphuric acid be placed with a few pieces of carbonate of baryta in two matrasses, and brought to a boiling-point; then with the end of a glass rod introduce into one of them a few drops of hydrochloric acid. A white powder will be seen to detach itself in increasing quantity from the pieces of carbonate, and at the same time an effervescence will take place owing to the disengagement of carbonic acid. In the other matrass nothing of the kind takes place; the liquid is hardly rendered turbid by a scarcely perceptible trace of sulphate of baryta.

In this case a similar phænomenon takes place as in the manufacture of white lead by the Dutch process, in which a trace of vinegar

is sufficient to determine the oxidation of an enormous quantity of lead. Without the agency of that acid the lead would not be acted upon by air or carbonic acid. In like manner, although in a lesser degree, carbonate of baryta resists the action of sulphuric acid without the presence of hydrochloric acid.

I thought that marble would be acted upon still more easily than carbonate of baryta by a mixture of diluted sulphuric acid and a small quantity of hydrochloric acid; but my experiments have given a result contrary to my expectations. Under the same conditions as those pointed out for carbonate of baryta, marble is acted upon with more difficulty and more slowly than the last named salt. The addition of a relatively large quantity of hydrochloric acid shortens very little the time it takes to be converted into sulphate of lime. The pieces of marble are deeply impregnated with sulphate of lime. I do not know the cause of this difference of action; but, at all events, I have been obliged to give up the hope which I entertained that marble and compact calcareous stones, under the influence of dilute sulphuric acid and a small quantity of hydrochloric acid, might produce an easy and regular disengagement of carbonic acid without being previously pulverized, which might have been turned to useful account by manufacturers of aërated waters.—*Comptes Rendus*, April 18, 1859.

Canouil's *Processes for manufacturing Chemical Matches without Phosphorus and containing no Poisonous Substance.*

1. *Mass without Phosphorus for Sulphured Matches.*

The matches without phosphorus manufactured in Paris by Canouil, are ignited by rubbing upon any hard body, whether it be rough or smooth, supposing the surface against which they are rubbed to present a certain amount of resistance.

Neither a blow, nor a shock, nor a temperature of 356° F. are capable of igniting these matches; their combustion is only caused by friction.

As the mass contains no phosphorus, their manufacture presents no danger for the workpeople, as they neither cause explosions, nor injurious emanations. The mass of these matches, which were patented in France in March 1857, contains the following substances:—

Dextrine	10 parts.
Chlorate of potash	75 „
Brown oxide of lead	35 „
Iron pyrites	35 „
Water, the quantity necessary to form a uniform paste.	

The chlorate of potash, the oxide of lead, and iron pyrites are separately powdered, and then made into a paste by means of the solution of dextrine; into this the ends of the sulphured matches are dipped in the usual way.

The dextrine might be replaced by gum or glue, and the iron

pyrites by other metallic sulphurets, to some of which, however, it is preferable as not being poisonous.

2. *Safety-matches with a peculiarly prepared Friction-surface.*

A second patent of Canouil's, dated October 7, 1857, relates to safety-matches of wood, wax, paper, German tinder, &c., which ignite only at a particular surface, containing no phosphorus. The latter consists of a slip of wood, card, or metal, covered with a layer of the preparation, which causes the ignition of the chemical match by mere friction. Such matches may be sent anywhere without the least danger, as the matches and the friction-surfaces may be packed in separate boxes. The mass for the matches consists of—

Chlorate of potash	7 parts.
Acetate of lead	2 „
Bichromate of potash	2 „
Flowers of sulphur	1 „
Gum or dextrine	6 „
Water	18 „

The covering for the friction-surface consists of—

Iron scales	1 part.
Emery	1 „
Chlorate of potash	6 „
Minium	1 „
Size, a sufficient quantity to form a paste, which is applied to a slip of card, wood, or metal.	

The substances in both formulæ are made into paste, as described for the first matches.

3. *New Mass without Phosphorus for Sulphured Matches.*

In order to avoid the slight explosions which occur on the friction of the first matches, the discoverer now leaves the metallic sulphurets or the sulphur out of the composition. They are replaced by powdered glass or flint, which is mixed in various proportions with the chlorate of potash, according as it is desired to produce combustion with more or less ease by friction. Bichromate of potash is also added as an oxidizing body.

The new mass for sulphured matches consists of—

Chlorate of potash	5 parts.
Powdered glass or flint	3 „
Bichromate of potash	2 „
Gum or dextrine	2 „
Water	8 „

Dingler's *Polytechn. Journal*, cli. p. 321.

Cleaning Paint Brushes from dried Oil Colours. By C. Brunner.

Having been frequently applied to by artists for a means of effecting this purpose, the author made a series of experiments, which led him to the following method:—

A solution of 1 part of crystallized carbonate of soda in 3 parts of water is prepared; the brushes to be cleaned are suspended in

this fluid contained in a cylindrical glass, so that they remain at a distance of about 2 inches from the bottom of the vessel, and the apparatus is left standing at a gentle heat (140°—158° F.) for 12—24 hours. A longer time will rarely be necessary. The dried colour is then so much softened, that it may be easily removed in the well-known manner with soap. Brushes dried as hard as a stone, may be rendered useful again by this process. It is essential that the above-mentioned temperature should not be exceeded, as otherwise the hairs, especially of hog-tools, are acted upon and entirely destroyed.—Dingler's *Polytechn. Journal*, cl. p. 379.

PROCEEDINGS OF SOCIETIES.

Royal Society.

Jan. 20, 1859. (Sir Benjamin C. Brodie, Bart., Pres., in the Chair.)

"Second Note on Ozone." By Thomas Andrews, M.D., F.R.S., and P. G. Tait, M.A., F.C.P.S.

Since the publication of their "Note on the Density of Ozone" (Chemical Gazette for August 15, 1857), the authors have been occupied with an extended investigation into the nature and properties of that body. The inquiry having proved more protracted than they anticipated, they have thought it proper to send to the Royal Society a brief notice of some of the more important facts which they have already observed, reserving a description of the methods employed, and of the details of the experiments, for a future communication.

The commonly received statement, that the whole of a given volume of dry oxygen gas contained alone in an hermetically sealed tube can be converted into ozone by the passage of electrical sparks, is erroneous. In repeated trials, with tubes of every form and size, the authors found that not more than $\frac{1}{100}$ part of the oxygen could thus be changed into ozone. A greater effect was, it is true, produced by the silent discharge between fine platina points; but this also had its limit. In order to carry on the process, it is necessary to introduce into the apparatus some substance, such as a solution of iodide of potassium, which has the property of taking up, in the form of oxygen, the ozone as it is produced. After many trials, an apparatus was contrived in the form of a double U, having a solution of iodide of potassium in one end, and a column of fragments of fused chloride of calcium interposed between this solution and the part of the tube where the electrical discharge was passed. The chloride of calcium allowed the ozone to pass, but arrested the vapour of water; so that, while the discharge always took place in dry oxygen, the ozone was gradually absorbed. The experiment is not yet finished, but already one-fourth of the gas in a tube of the capacity of 10 cubic centimetres has disappeared. To produce this effect, the discharge from a machine in excellent order has been passed through the tube for twenty-four hours.

When oxygen is thus converted into ozone, a diminution of volume takes place. The greatest contraction occurs with the silent discharge,

and amounts to about $\frac{1}{35}$ of the volume of the gas. The passage of sparks has less effect than the silent discharge, and will even destroy a part of the contraction obtained by means of the latter. If the apparatus be exposed for a short time to the temperature of 250° C., so as to destroy the ozone, it will be found that the gas on cooling has recovered exactly its original volume. This observation proves, unequivocally, that if ozone be oxygen in an allotropic condition, its density is greater than that of oxygen. Experiments still in progress indicate that the density of ozone obtained by the electrical discharge must, on the above assumption, be represented by even a higher number than that deduced by the authors from their experiments on ozone prepared by electrolysis.

When mercury is brought into contact with dry oxygen, in which ozone has been formed by the electrical discharge, it loses to a great extent its mobility, and may be made to cover the interior of the tube with a fine reflecting surface resembling that of an ordinary mirror. It is remarkable that this great change in the state of the mercury is not accompanied by any further diminution of the volume of the gas. The apparatus employed by the authors would have enabled them to estimate with certainty a change of volume amounting to $\frac{1}{12000}$ part of the whole. On the contrary, on allowing the apparatus to stand, the gas begins slowly to expand; and in thirty hours, when the ozone reactions have disappeared, the expansion amounts to a little more than one half of the contraction which had previously taken place.

Dry silver, in the state both of leaf and of filings, has the property of entirely destroying ozone, whether prepared by electrolysis or by the electrical machine. If a stream of electrolytic ozone be passed over silver leaf or filings contained in a tube, the metal becomes altered in appearance where the gas comes first into contact with it; but no appreciable increase of weight takes place, however long the experiment may be continued. The volumetric results are similar to those already described in the case of mercury.

Arsenic also destroys dry ozone, but, as it likewise combines with dry oxygen, its separate action on ozone cannot be observed with precision.

Most of the other metals examined, such as gold, platina, iron, zinc, tin, &c., are without action on dry ozone.

Iodine, brought into contact with oxygen contracted by the electric discharge, instantly destroys the ozone reactions, and a yellowish solid is formed: no change of volume accompanies this action.

Peroxide of manganese and oxide of copper have, it is well known, the property of destroying ozone, apparently without limit. The authors have found that these oxides undergo no sensible increase of weight, even after the destruction of 50 or 60 milligrammes of ozone. The same oxides, when brought into contact with oxygen contracted by the spark, restore it to nearly its original volume.

Hydrogen gas, purified with care, and perfectly dry, was not changed in volume by the action either of the electrical spark, or of the silent discharge.

A similar negative result was obtained with nitrogen and the silent

discharge; but with the spark a very slight alteration of volume appeared to occur, the cause of which is still under investigation.

In the experiments now described, the electrical sparks and discharge were always obtained from the common friction-machine. The discharge from the induction coil, even when passed through two Leyden jars, produces very insignificant ozone effects. The heat which always accompanies this discharge, and its comparatively feeble tension, sufficiently explain its want of energy.

All the results recently obtained by the authors fully confirm the former experiments of one of them*, that in no case is water produced by the destruction of ozone, whether prepared by electrolysis or by the electrical discharge. They reserve any further expression of their views as to the true relations which exist between ozone and oxygen, till they shall have an opportunity of laying the results of this inquiry in a more complete form before the Society.

Jan. 27, 1859. (Sir Benjamin C. Brodie, Bart., Pres., in the Chair.)

"Researches on a New Class of Organic Bases, conducted by Charles S. Wood, Esq." By A. W. Hofmann, LL.D., F.R.S.

In his remarkable memoir† on the action of reducing agents on nitro-compounds, in which Zinin first pointed out the formation of organic bases by the substitution of hydrogen for oxygen, some experiments are recorded on the deportment of dinitronaphtaline (nitronaphtalese) with sulphuretted hydrogen. Zinin states that this process gives rise to the formation of a basic compound crystallizing in delicate copper-red needles, and yielding with acids white scaly salts.

In a subsequent paper‡ Zinin returns to the action of sulphuretted hydrogen on dinitronaphtaline, and gives a fuller account of the products obtained in this process. The basic substance arising from dinitronaphtaline crystallizes in colourless needles of great brilliancy, which contain

$$C_{10}H_5N, \text{ or } C_{20}H_{10}N_2.$$

It is a well-defined basic body, which Zinin describes under the name of seminaphlalidam. From this later communication it would appear that the copper-red coloration originally observed was due to the presence of a foreign colouring matter, which can be separated by crystallizing the base alternately from alcohol and water.

Subsequently the copper-red body appears to have been observed by Laurent§, who states that the action of sulphuretted hydrogen upon dinitronaphtaline gives rise to the formation of a carmine-red alkali. He did not, however, analyse this substance, and the discovery of nitraniline‖ having established the existence of basic nitro-substitutes, the compound in question was hitherto believed to be nitro-naphtylamine.

The red crystals have of late been minutely investigated in my laboratory by Mr. Charles Wood, whose experiments have led to an unexpected result, which I beg to lay before the Society.

* Philosophical Transactions for 1856, Part I.
† Bulletin Scientifique de St. Pétersburg, x. 18.
‡ Journ. für Prakt. Chem. Bd. xxxiii. 29.
§ Compt. Rend. xxxi. 538.
‖ Muspratt and Hofmann, Memoirs of the Chemical Society, vol. iii. 111.

A current of sulphuretted hydrogen transmitted through a boiling solution of dinitronaphtaline in weak alcoholic ammonia slowly reduces the nitro-compound. The process is continued for two or three hours, during which time the greater part of the spirit distils off; the residue is acidified with dilute sulphuric acid, and the liquid heated to ebullition. The filtered liquid deposits on cooling a yellowish brown sulphate, which may be purified by several crystallizations from boiling water. The addition of ammonia to the solid sulphate immediately changes the colour to a fine dark carmine-red; the base thus liberated is washed with cold water, and finally purified by crystallization from water or very dilute alcohol.

Thus prepared, the substance, for which Mr. Wood proposes the name *ninaphtylamine*, is a light flocculent mass, composed of little acicular crystals, which are partially decomposed by exposure to a temperature of 100° C. It is difficultly soluble in boiling water, but extremely soluble in alcohol and ether.

In the analysis of the base dried *in vacuo* over sulphuric acid, Mr. Wood has obtained results which lead to the formula

$$C_{20} H_8 N_2 O_2.$$

This expression was confirmed by the examination of several of the salts of the new base.

Sulphate of ninaphtylamine is obtained either by recrystallizing the crude salt formed in the preparation of the body, or by dissolving the pure base in dilute sulphuric acid. It forms white scales, which are apt to be decomposed by recrystallization from pure water. The salt dried *in vacuo* over sulphuric acid contains

$$2(C_{20} H_8 N_2 O_2), \quad H_2 S_2 O_8.$$

Hydrochlorate of ninaphtylamine forms acicular crystals; they are obtained like the sulphate, which they resemble in their general deportment. Composition:

$$C_{20} H_8 N_2 O_2, H Cl.$$

The *platinum-salt of ninaphtylamine* forms rather soluble yellowish-brown crystals, which are obtained by adding a concentrated solution of dichloride of platinum to an alcoholic or ethereal solution of the base. It has the usual constitution, containing

$$C_{20} H_8 N_2 O_2, H Cl, Pt Cl_2.$$

If it be permitted, in the absence of further experimental evidence, to speculate upon the molecular constitution of the body which forms the subject of this note, the simplest interpretation of its composition and formation would be to view it as a substitution-product of naphtylamine, but differing from the ordinary nitro-substitutes, by containing the elements of binoxide, instead of tetroxide of nitrogen.

$$\text{Naphthylamine} \quad \therefore C_{20} H_9 N = \left.\begin{matrix} C_{20} H_7 \\ H \\ H \end{matrix}\right\} N,$$

$$\text{Ninaphthylamine} \quad \therefore C_{20} H_8 N_2 O_2 = \left.\begin{matrix} C_{20} (H_6 NO_2) \\ H \\ H \end{matrix}\right\} N.$$

Its formation would then be represented by the equation

$$\underbrace{C_{20}[H_6(NO_4)_2]}_{\text{Dinitronaphtaline.}} + 4\,H_2S_2 = 3\,H_2O_2 + 8\,S + \underbrace{C_{20}[H_8NO_2]N}_{\text{Ninaphthylamine.}}$$

Bodies in which binoxide of nitrogen figures as a material of substitution are as yet extremely rare, whilst nitro-substitutes containing the elements of hyponitric acid are of the most general occurrence.

Some chemists have considered nitrous ether as a binoxide of nitrogen derivative of alcohol.

Alcohol ..... $C_4H_6O_2$,

Nitrous ether ..... $C_4\left(\begin{matrix}H_5\\NO_2\end{matrix}\right)O_2$.

The most interesting illustrations of this kind of substitution, however, have been furnished by Messrs. Church and Perkin* in the colouring matters produced by the action of nascent hydrogen on dinitro-substitutes, or of nitrous acid upon certain monamines.

Phenylamine ..... $C_{12}H_7N$.

Nitrosophenyline ..... $C_{12}\left(\begin{matrix}H_6\\NO_2\end{matrix}\right)N$.

Naphthylamine ..... $C_{20}H_9N$,

Nitrosonaphtyline ..... $C_{20}\left(\begin{matrix}H_3\\NO_2\end{matrix}\right)N$.

Expressed by these formulæ, the substances in question appear to be closely allied to Mr. Wood's base; in fact, nitrosonaphtyline has the same composition as ninaphthylamine. But a superficial comparison of the properties of the two bodies excludes any idea of their being identical. The formulæ of nitrosophenyline and nitrosonaphtyline have not as yet been finally established by the analysis of their compounds, these substances, like colouring matters in general, being of an indifferent character. It is probable that they are formed by the association of several molecules, a supposition which receives considerable support from the discovery of ninaphthylamine.

The formation of ninaphthylamine promises to add considerably to the number of nitro-derivatives of the aromatic monamines. To each of these substances probably corresponds a nitrous and a nitric substitution-base, but as yet we are unacquainted with a single one in which both derivatives are known, as shown by a glance at the groups best examined.

Phenyle Group.			Naphtyle Group.		
Phenylamine....	$C_{12}H_5$ H H	N,	Naphthylamine	$C_{20}H_7$ H H	N.
Unknown ..	$C_{12}(H_4NO_2)$ H H	N,	Ninaphthyl-amine....	$C_{20}(H_6NO_2)$ H H	N.
Nitrophenyl-amine...	$C_{12}(H_4NO_4)$ H H	N,	Unknown	$C_{20}(H_6NO_4)$ H H	N.

* Journal of Chemical Society, vol. ix. 1.

THE CHEMICAL GAZETTE.

No. CCCC.—June 15, 1859.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Colouring Matter of the Bile and its Detection.
By E. Brücke.

In last December, Dr. Valentiner stated in Günzburg's 'Zeitschrift,' that from gall-stones, bile and the livers, and frequently other tissues of jaundiced patients, a crystalline substance may be obtained by means of chloroform, which differs from previously known colouring matters of the bile, and agrees in all its properties with hæmatoidine. The solution in chloroform, when treated with nitric acid, gave in a remarkably beautiful manner the well-known series of colours of Gmelin's bile-test; on the contrary, after the removal of the matter soluble in chloroform, the bile, which was still of a dark green colour, showed no trace of the reaction. Dr. Valentiner, therefore, proposed that when it is necessary to detect small quantities of the colouring matter of bile in a fluid, the latter should be agitated for a long time with chloroform, and the solution in chloroform, after separation, directly treated with nitric acid. The author repeated this experiment, and agitated the contents of a number of human gall-bladders with chloroform, poured the bile as completely as possible from the specifically heavier menstruum, which was now of a yellow colour, and filtered the latter through a double paper filter which retained the residue of the bile. The filtrate was poured into a retort and the chloroform slowly distilled off in the water-bath, without being allowed to boil. The residue, when cold, was treated with alcohol of spec. grav. 0·831; the crystals partly adhered to the interior of the retort, and partly sank after agitation with the alcohol, in the form of a red dust. The alcohol was poured away, and the crystals removed as completely as possible, and purified by decantation with alcohol and æther.

The author took a portion of the bile poured away from the chloroform, and evaporated it to dryness in the water-bath; the

residue he powdered, and extracted with chloroform, which he then separated by filtration; he then returned the residue of the filtration into a bottle, treated it again with chloroform, and added so much water to it that the dry bile dissolved again. He then extracted further by agitation, renewing the chloroform from time to time; the quantity of colouring matter taken up constantly diminished, and the changes of colour which it exhibited with nitric acid became gradually weaker, and at last imperceptible. Of the bile now poured away, a small quantity diluted with much water, was submitted to Gmelin's test; it exhibited the change of colour very beautifully, even when the author employed dilute nitric acid, and then added concentrated sulphuric acid, which sinks to the bottom and causes the process of decomposition to take place from the bottom, so that the whole of the colours may be observed simultaneously in superimposed strata. Even with this modification of Gmelin's bile-test, which is due to Brücke, he obtained the same positive result.

This fact was in evident contradiction to Dr. Valentiner's statement. The bile exhausted by chloroform formed green solutions with water; these were not rendered yellow by the addition of potash, but only a little more yellowish green; by muriatic acid more bluish green. The author consequently supposed that probably of the two colouring matters, known as biliphæine and biliverdine, which are the objects of Gmelin's test, one, biliphæine, is soluble in chloroform and the other not, and it therefore became of importance to ascertain whether the crystals obtained from chloroform were not crystallized biliphæine, or a crystallized compound of biliphæine. This would by no means exclude its identity with hæmatoidine, which is contended for by Dr. Valentiner. Eleven years ago Virchow called attention to the analogies with biliphæine (cholepyrrhine) which his hæmatoidine presented under the action of certain reagents.

Virchow, indeed, comes to the conclusion that his hæmatoidine is distinct from biliphæine; nevertheless he says that, although in the present state of chemistry the differences are sufficient for a distinction, still they are by no means absolute, but rather to be referred to difference in cohesion, nay, that an extraordinary similarity between the two colouring matters cannot be denied. He regards it as most probable that the colouring matter of the blood becomes gradually converted into colouring matter of the bile, and that hæmatoidine is a member of the series of these products of metamorphosis (Arch. für Path. Anat. i. p. 421).

The author therefore immediately prepared a fresh quantity of crystals; dissolved them, after purification, in ammonia, and then added dilute muriatic acid thereto until the fluid had an acid reaction. It became turbid, and on shaking the turbidity collected into yellowish-brown flakes, from which the fluid was separated in a perfectly colourless state by filtration. Under the microscope these flakes appear of a yellow colour, and perfectly amorphous. When rapidly washed with distilled water, they exhibited in their

behaviour with reagents the characters of biliphæine, as indicated by Heintz.

In the same way their alkaline solutions absorbed oxygen from the air, and acquired a green colour owing to the formation of biliverdine.

The point now was to ascertain whether the crystals had undergone any chemical change by solution in ammonia and precipitation by muriatic acid, or whether they could be obtained by mere solution of the biliphæine in chloroform and evaporation of the latter. The very first experiment decided the point in the second way. As the amorphous biliphæine had been all used in testing its behaviour with reagents, a fresh and larger quantity of crystals was dissolved in ammonia, precipitated with muriatic acid, filtered, and washed. During the operation, a portion of the biliphæine was converted into biliverdine, so that the residue of filtration was of a greenish colour. It was placed immediately after being washed, and while still moist, in chloroform, in which it was dissolved by shaking with the aid of a gentle heat. The fluid was of a yellowish-green colour, but when it was filtered it became yellow. At the bottom of the filter there remained a green deposit, whilst its margin, where the solution had spread under evaporation of the solvent, had an orange-yellow colour. The biliphæine alone, therefore, was dissolved in the chloroform, and the biliverdine was mechanically suspended in it.

The chloroform was distilled from the yellow solution; the residue was again found to be crystalline almost throughout, only a small quantity of the biliphæine remaining amorphous.

Chloroform, recommended by Valentiner, is therefore an admirable means of extracting biliphæine, one of the objects of the test for the colouring matter of the bile; biliverdine is insoluble in it. By this means chloroform furnishes us with the means not only of preparing biliphæine easily in a pure state, but also of extracting it from a mixture with biliverdine, and thus purifying the latter. On the other hand, biliverdine may be extracted from biliphæine by alcohol, in which the former dissolves with ease, whilst biliphæine is difficult of solution in it. Pure biliverdine may also be prepared from the red crystals, by dissolving them in an aqueous solution of carbonate of soda, and leaving the solution to absorb oxygen from the air, as indicated by Heintz; lastly, precipitating with muriatic acid, washing out the filtrate, and removing any residue of biliphæine by means of chloroform. — *Sitzungsber. der Akad. der Wiss. zu Wien*, xxxv. p. 13.

On the Occurrence of Tagilite *and* Libethenite, *as well as some Combinations of Lime, Copper, and Phosphoric Acid, in a Mine near Coquimbo, Chili. By* Frederick Field, Esq., F.C.S.*

In the mine 'Mercedes,' about twenty miles east of Coquimbo, Chili, there exists a large quantity of apatite in crystals of con-

* Communicated by the Author.

siderable size imbedded in black oxide of iron. The mine is worked for copper, and frequently the apatite traverses considerable masses of copper-pyrites, intermingled with black magnetic iron-ore. The crystals of apatite found in the deeper parts of the mine are not particularly remarkable, containing merely traces of chlorine with from 3 to 5 per cent. of chloride of calcium.

Nearer the surface, however, there are large crystals imbedded in brown iron-ore having a pale green colour due to oxide of copper, and containing from 1 to 2 per cent. of water. These crystals I have observed in very large quantities in the same mineral district. All my analyses prove the presence of oxide of copper and water, together with a small per-centage of chloride of calcium. The occurrence of hydrous apatite is rare. In the 5th supplement of 'Dana's Mineralogy,' a paper is quoted from M. Damour, giving an account of a hydroapatite from the Pyrenees, found in the fissures of a brown ferruginous rock. The analysis yielded—

Phosphoric acid	40·00
Lime	47·31
Fluoride of calcium	6·96
Water	5·30
Phosphate of iron	43
	100·00

and the same schist affords Wavellite.

I have found many crystals in a mine near Coquimbo of a light turquoise-blue colour, rather inclining to green. These, upon examination, were proved to contain a considerable proportion of copper, and may be considered as consisting of a double phosphate of copper and lime.

One very pure specimen yielded—

Oxide of copper	20·93
Phosphoric acid	37·69
Lime	36·64
Chloride of calcium	2·33
Water	2·32
	99·91

A mineral consisting of 2 atoms of phosphochalcite, 10 atoms of tribasic phosphate of lime, and 1 atom of chloride of calcium would require nearly the same numbers, and would be expressed by the following formula—

$$2(6\,CuO, PO^5\,3\,HO) + 10(3\,CaO, PO^5) + CuCl,$$

or in 100 parts—

2 Phosphochalcite ($6\,CuO, PO^5\,3\,HO$)	29·56
10 Tribasic phosphate of lime, $3\,CaO, PO^5$	68·03
1 Chloride of calcium	2·39
	99·98

That the copper exists in the state of phosphate and not simply as oxide, is rendered evident by the action of ammonia upon the

solution of the mineral in weak nitric or hydrochloric acid. A copious precipitate of phosphate of lime takes place with solution of phosphate of copper. Addition of sulphate of magnesia to the filtrate, immediately produces a crystalline deposit of ammonio-magnesia phosphate.

The rare mineral *Tagilite*, found originally in Nischne-Tagilsk in the Ural, and first investigated by Hermann, is also found in specimens of considerable purity and beauty in the 'Mercedes,' forming stellated and fibrous masses upon brown iron-ore. The following are analyses, one from Nischne-Tagilsk, and the other from Coquimbo:—

	From Nischne-Tagilsk (Hermann).	From Coquimbo.
Oxide of copper ..	61·80	61·70
Phosphoric acid ..	27·70	27·42
Water	10·50	10·25
	100 00	99·37

or $4CuO, PO^5 + 3HO$.

Libethenite is also found in the same mine, although in less abundance than Tagilite, having a dark olive-green colour sometimes approaching to black, and a resinous or rather waxy surface.

100 parts gave—

Oxide of copper	66·42
Phosphoric acid	29·31
Water	3·74
	99·47

corresponding very closely to

$$4CuO, PO^5 + HO,$$

or Tagilite minus 2 atoms of water.

Guayacan, Coquimbo, April 11, 1859.

On the Preparation of Metallic Cobalt. *By* William Sharswood.

The attention of the author was attracted to this subject owing to a necessity of obtaining the element for the purpose of making researches in thermo-electricity.

The source from which the author recommends the metal to be obtained is the chloride of purpureocobalt*, from the fact of its presenting the means by which a pure chloride of cobalt can be obtained with comparatively most ease and certainty.

The formation of the chloride of purpureocobalt is effected by simply oxidizing the chloride of cobalt with ammonia by exposure to the air.

It is not necessary to use a pure chloride of cobalt in forming the chloride of purpureocobalt; any commercial oxide answering, even in the presence of arsenic, nickel, iron, and other impurities.

* Researches on the Ammonia-Cobalt Bases, by Walcott Gibbs and Fred. Aug. Genth, Chemical Gazette, vol. xv. p. 188.

A perfectly pure chloride of cobalt is easily prepared from this salt by heating it in a porcelain crucible until vapours of ammonia and chloride of ammonium cease to be driven off. The pure anhydrous chloride of cobalt thus obtained is characterized by beauty of colour, forming pale blue talcose scales.

To obtain the metal in a state of sponge, it is merely necessary to reduce the chloride by means of hydrogen*. In order to fuse the metal, it is an indispensable precaution, to preserve its purity, that it be effected by means of the *lime crucibles* as employed by M. Sainte-Claire Deville. In connexion with these crucibles, he uses a lamp of peculiar construction, in which the vapour of any liquid hydrocarbon, as oil of turpentine, is completely consumed by means of an artificial blast of air. By means of this instrument the fusion of felspar can be accomplished with facility. It has been found that the platinum metals fused in *these crucibles*, present properties very different from those heretofore attributed to them, the lime serving to deprive them of osmium and silicon.

As much carbon becomes mixed with cobalt in the ordinary method of fusion, one of its characters, that of malleability, becomes entirely destroyed; and a piece of the metal thus prepared, when placed before the oxyhydrogen blowpipe, upon a brick, in which a groove had been cut for the purpose of obtaining it in the form of a bar, merely assumed an intumescent state, without exhibiting any tendency to enter the incision.

Since this, M. Debray has found that pure molybdenum completely withstands the temperature at which platinum, &c. become liquid; and that its melting-point, in a crucible of carbon before the oxyhydrogen blowpipe, is at a temperature at which rhodium fuses. He further states, however, that the fused mass was contaminated with from 4 to 5 per cent. of carbon.—*Proc. Charleston Nat. Hist. Soc.*

On the Production of Pictures by means of Iodine and Guaiacum Resin. By L. E Jonas.

The property of vapours of iodine, when they pass over any surface, of depositing themselves in the form of fine crystals of iodine upon all elevations, has been employed by the author in producing impressions of lithographs, &c. If a picture of this kind be exposed to vapour of iodine, and then pressed upon a paper moistened with tincture of guaiacum, a blue copy is obtained. To produce a good result, the following things are requisite :—

1. A paper of peculiar strength, evenness, firmness and smoothness, and quite free from starch.

2. An alcoholic solution of guaiacum, which especially possesses the property of acquiring a blue colour (1 part of resin and 32 parts of alcohol).

3. The maintenance of a definite degree of moisture at the moment of pressure, and the coating of the paper with the solution of guaiacum.

* The preparation from the oxalate will be treated of hereafter.

4. Powerful pressure upon the original, which must be sufficiently iodized to allow the iodine to penetrate the paper.

The more delicate and clear the picture or writing which is to be copied, the better is the result. Other objects which present distinct elevations and flat surfaces may be printed from by suitable arrangements; this is especially the case with parts of plants, as in the well-known nature-printing.—*Journal für Prakt. Chemie*, lxxv. p. 244.

On Hæmatoxyline. By O. L. Erdmann.

The following experiments were made by O. Hesse in Erdmann's laboratory. The hæmatoxyline was prepared by Erdmann's method by means of aqueous æther. By subsequent recrystallization from water, to which a little sulphite of ammonia or soda is added, it is obtained in perfectly colourless crystals. These contain more or less water of crystallization, as was previously stated by the author. Crystals with a larger quantity of water of crystallization were analysed; the analyses agreed well with the formula given by Gerhardt, $C^{32}H^{14}O^{12}+6HO$,—

	Found.	Calculated from $C^{40}H^{17}O^{15}$.	Calculated from $C^{32}H^{14}O^{12}$.	Previous experiments of Erdmann.				
C	63·21	63·67	63·57	63·19	63·62	63·72	63·66	63·17
H	4·68	4·51	4·63	4·65	4·70	4·69	4·68	4·70
		$C^{40}H^{17}O^{15}+8HO$.	$C^{32}H^{14}O^{12}+6HO$.					
Water of crystallization	15·30	16·03	15·17	16·37	16·51	16·09		

If a solution supersaturated at ordinary temperatures be left standing, larger crystals are obtained in time; these usually have smooth faces which are sometimes strongly curved.

The crystals with a smaller quantity of water of crystallization were determined by Naumann. They belong to the rhombic system. The amount of water found was=5·40, 5·53, 5·61 per cent., the formula requires 5·62 per cent.

When hæmatoxyline is treated with boiled solution of potash in an atmosphere of hydrogen, it is but slightly coloured even by boiling. When saturated with sulphuric acid, the fluid becomes red; but white hæmatoxyline may be obtained from it again. Carbonate of soda behaves in the same way. Yeast (in a few days at 86° F.) or emulsine (in 6 hours at 113° F.) colours the solution of the substance red; it then contains some hæmateine besides hæmatoxyline. Even concentrated muriatic acid effects no essential decomposition.

Hæmatoxyline reduces Fehling's solution. It diverts the plane of polarization strongly to the right. The experiments show for 1 grm. $C^{32}H^{14}O^{12}$ in 100 grms. of water, with a length of tube of 200 millims., an average of $-1°{\cdot}85$ to the right.

Hæmatoxyline is soluble in a cold saturated solution of borax

until it comes to the consistence of a syrup. From a solution of this kind the colouring matter cannot be recovered in a crystalline form by evaporation. By taking up hæmatoxyline, the solution of borax loses its basic reaction, and afterwards has either a neutral or weakly alkaline reaction upon litmus-paper. The borax cannot be precipitated from such a solution by absolute alcohol, or by a mixture of absolute alcohol and æther. It exhibits a bluish fluorescence.

If a few drops of muriatic acid be let fall into this fluid, a violent movement is observed in it, and in 10—20 seconds the entire fluid is converted into a dense crystalline mass. The vessel may then be turned upside down, without the mother-liquor flowing out. But within a few hours a conversion of the crystals commences; granular crystals make their appearance, and settle to the bottom of the vessel, and above them there is a large quantity of fluid. These granular crystals consist of $C^{32}H^{14}O^{12}+2HO$. Sulphuric acid and acetic acid behave in the same way as muriatic acid. If, on the other hand, a concentrated solution of chloride of sodium be dropped into such a solution, each drop sinks to the bottom enveloped in an amorphous mass. In this way many drops of solution of chloride of sodium may be seen depositing themselves one upon the other in the boracic solution. If the fluid be stirred round, a slimy, emulsive fluid is produced, from which a tenacious mass is deposited in a short time. This possesses a silky lustre, which is caused by small cavities. The mass, which is at first but slightly coloured, soon becomes red, as it is very sensitive to light and ammonia. It dissolves pretty readily in boiling water or alcohol, but separates in its previous form on the cooling of the solution. It consists of amorphous hæmatoxyline, and this may perhaps be the reason why solution of hæmatoxyline in biborate of soda produces a greater or less deviation in polarized light. A similar behaviour to that of chloride of sodium is also exhibited by the chlorides of potassium and ammonium, ferrocyanide of potassium, and bisulphite of ammonia, but chloride of sodium gives the most beautiful precipitate. Oxalate of potash, and sulphate, phosphate, and carbonate of soda produce no precipitates. Bisulphite of ammonia dropped into the solution of hæmatoxyline in borax, immediately produces a slimy precipitate. This disappears when the solution is boiled, but separates again in its characteristic form on its cooling. By continued dropping of bisulphite of ammonia into the syrupous fluid, the point is soon reached at which the amorphous hæmatoxyline disappears. Crystals of hæmatoxyline are then very soon obtained. If amorphous hæmatoxyline be dissolved in boiling water, and a drop of muriatic acid be added to it, so that a distinctly acid reaction is produced, crystals are very soon obtained, usually with 2HO.

Hyposulphite of soda when heated dissolves considerable quantities of crystallized hæmatoxyline; the solution has a purple colour, and on cooling deposits amorphous hæmatoxyline, which appears somewhat coloured.

Hæmatoxyline is rather difficult of solution in solution of chloride of sodium, but dissolves more readily in solution of chloride of barium. From the latter fluid crystals of $C^{32}H^{14}O^{12}+6HO$ separated, but in the course of 24 hours these had become completely transformed into $C^{32}H^{14}O^{12}+2HO$. Phosphate of soda, $\left.\begin{matrix}(NaO)^2\\HO\end{matrix}\right\}PO^5$, is capable of dissolving a large quantity of hæmatoxyline, and behaves very like the solution of borax, but retains its basic reaction. When carefully employed, it but slightly reddens hæmatoxyline.—*Journal für Prakt. Chemie*, lxxv. p. 218.

On Phosphuret of Chromium. *By* C. A. Martius.

A mixture of oxide of chromium, phosphoric acid, and lamp-black, when put into a charcoal crucible and exposed to the heat of a furnace with a strong draught, furnished a grayish-black mass, which was easily pulverized, and when extracted with muriatic acid left a gray metallic powder. The same experiment, repeated in a Sefström's blast-furnace, furnished, besides an unfused gray mass, some small, brittle, very hard metallic globules of an iron-gray colour, and of only 4·68 spec. grav. It appears therefore that phosphuret of chromium is not to be prepared in this way in a crystalline form, and that it is very difficult of fusion. It is most easily obtained in the form of a powder by heating chromate of potash to redness in a tube of Bohemian glass, and passing over it the vapour of some phosphorus placed in the closed end of the tube. Vivid incandescence is produced, and a black mass is obtained, which after lixiviation with water, leaves the phosphuret of chromium in the form of a fine crystalline metallic powder.

The phosphuret, prepared in either way, is insoluble in any acids. When heated in chlorine gas it burns rapidly, forming chloride of phosphorus and crystalline violet perchloride of chromium. In oxygen gas it burns away to form green phosphate of chrome. When fused with hydrate of potash, it is oxidized with evolution of hydrogen gas. When thrown into fusing chlorate of potash, it burns with a very vivid incandescence and evolution of chlorine gas. Fusing nitrate of potash does not act so violently. Its analysis gave 62·5 per. cent of chromium, and 34·5 per. cent of phosphorus, according to which this compound has the formula Cr^2P, that is to say, the same as that of the phosphuret of chromium prepared by H. Rose by the decomposition of perchloride of chromium with phosphuretted hydrogen.—Liebig's *Annalen*, cix. p. 82.

ANALYTICAL CHEMISTRY.

Volumetric Determination of Phosphoric Acid by means of Acetate of Uranium. *By* Dr. Pincus.

The volumetric determination of phosphoric acid by oxide of uranium is founded upon the constant compounds, discovered by

Werther, Knop, and Arendt, into which cPO^5 enters with oxide of uranium under certain circumstances, and upon their insolubility in acetic acid. Knop and Arendt have demonstrated that when solution of acetate of uranium is brought in contact with a solution containing cPO^5, with no other free acid except acetic acid, a constant compound, insoluble in acetic acid, is produced, the composition of which is represented by the formula $(Ur^2O^3)^2+PO^5$. In precise accordance with the assumed atomic weight of oxide of uranium=59·4, this compound, when calcined, is found to contain in 100 parts just 20 parts PO^5 and 80 parts Ur^2O^3; and they also found that the last traces of PO^5 are precipitated in the form of this constant compound. When ammoniacal salts are present ammonia also passes into the precipitate, forming a compound corresponding with phosphate of ammonia and magnesia; this, however, has no effect upon the final result, as in this case, as with the magnesia salt, the ammonia is volatilized by calcination.

Upon this, as is well known, Knop has founded a method of determining phosphoric acid by weighing, which is equally convenient and accurate, when a solution in which phosphoric acid is present contains, besides alkalies, alkaline earths, such as lime, magnesia, baryta, and oxide of iron; but his hope that the method would also prove applicable in the presence of alumina, has not been fulfilled.

The author has endeavoured to discover a volumetric method, in order by this means to enable phosphoric acid to be determined more easily and rapidly; for this purpose he recommends the following process:—

1. A solution of phosphate of soda or ammonia, the amount of PO^5 in which is accurately known, must be prepared: it is advisable to prepare this by a preliminary determination of the phosphoric acid in the ordinary way, and dilution with water, so that each cubic centim. may exactly represent 0·01 grm. PO^5; in this there is no difficulty.

2. A solution of acetate of uranium. This must be free from protoxide. The author found that by the employment of impure acetic acid containing empyreumatic products, some protoxide of uranium is readily formed, which the solution should not contain. (The pure solution of acetate of uranium evolves carbonic acid when exposed to the rays of the sun, and deposits a greyish-green precipitate. The solution of acetate of uranium, if it is to be kept free from protosalt, must be protected from the light.—*Knop.*)

The author determines the strength of the solution by pouring 5—10 cubic centims. of the solution of phosphoric acid into a beaker, adding some ammonia and an excess of acetic acid, and pouring the solution of uranium from a burette with divisions of $\frac{1}{10}$th—$\frac{1}{20}$th cubic centim., stirring the mixture frequently during the process. The well-known slimy precipitate of phosphate of uranium and ammonia is produced. From time to time a drop of the mixture is put upon a white porcelain plate, close to a small

drop of solution of ferrocyanide of potassium, and the two drops are allowed to flow together; as long as the PO^5 is not all precipitated, only a bluish-green colour is produced; but when the smallest excess of oxide of uranium is present, the spot, which is at first bluish green, becomes very beautifully and distinctly surrounded with a darker or lighter chocolate-coloured border; it is, however, to be observed that sometimes, especially with dilute solutions, the reaction disappears again in a few minutes after strong stirring; a further quantity of the solution of uranium is then to be added. If the brownish-red colour has remained permanent for ten minutes, it does not again disappear, but makes its appearance still more distinctly and beautifully, without any intermixture of yellow and green, when, after the settlement of the slimy precipitate, a drop of the clear supernatant fluid is employed for the reaction. When it has been exactly ascertained by repeated experiments how many cubic centims. of the solution of uranium are necessary for the precipitation of 0·05 or 0·10 grm. PO^5, we may, by calculation, and by adding water to the solutions, bring the solution of oxide of uranium nearly to such a state of dilution, that each cubic centim. thereof may precipitate the PO^5 contained in 1 cubic centim. of that solution, namely 0·01 grm. By repeated experiment, and by the addition of small quantities of water, or of a concentrated solution of oxide of uranium, it may be easily managed that the two solutions may be equivalent within the limits of $\frac{1}{10}$th—$\frac{1}{20}$th cubic centim. for quantities of 10—20 cubic centims., so that the highest possible error may lie within the limits of 0·0005—0·001 grm. PO^5. By great care even these limits may be still further contracted.

The employment of acetate of uranium for the volumetric determination, and of ferrocyanide of potassium for indicating the completion of the reaction, is exactly analogous to that of peroxide of iron in the well-known volumetric determination of phosphoric acid by means of a solution of peroxide of iron. The advantage of the process with oxide of uranium over that with oxide of iron, consists in the fact that in the former a filtration is unnecessary, because the yellow compound of phosphoric acid and oxide of uranium is not decomposed by ferrocyanide of potassium. If a drop of the fluid containing suspended phosphate of uranium be placed upon a white porcelain plate, and a drop of a dilute solution of ferrocyanide of potassium be added to it, the colour does not change instantaneously unless an excess of oxide of uranium be present: it is only very gradually that the decomposing action of the free acetic acid upon the ferrocyanide of potassium produces a bluish-green colour, but never a reddish-brown one; the reddish-brown colour makes its appearance immediately, however, when the mixture contains even an incredibly small excess of acetate of uranium; by this means the test is rendered far more convenient and the reaction more accurate than when, in accordance with Liebig's method, the fluid is first filtered through a doubled paper, and then dropped upon another paper soaked with ferrocyanide of potassium. As regards

the sensibility of the reaction, it may be remarked that a fluid containing only $\frac{1}{25000}$ to $\frac{1}{30000}$ of its weight of Ur^2O^3, exhibits the characteristic spots very beautifully and distinctly with ferrocyanide of potassium upon a porcelain plate; a clear fluid which contains $\frac{1}{100000}$, acquires a strong reddish-brown colour in a glass.

If the phosphoric acid in a fluid is to be determined, it is mixed, whether neutral or acid, with ammonia, acetate of soda, and then with acetic acid in excess. Any undissolved perphosphate of iron (protoxide of iron and alumina must not exist in the solution) is removed by filtration, and the process is then applied as above described. Every $\frac{1}{10}$ cubic centim. of solution of oxide of uranium employed until the production of the reaction represents 0·001 grm. PO^5. Heating the solution containing PO^5 facilitates the deposition. If it be desired subsequently to make an analysis by weight as a check upon the former, the same mixture is treated, with the addition of more oxide of uranium, in the manner described by Knop and Arendt. If too much oxide of uranium has been added in the volumetric analysis, and the experiment cannot be repeated from want of material, about 5 cubic centims. of the normal solution of PO^5 are added, and a reversed volumetric determination is made in the usual way.

It may be mentioned here in conclusion, as a precaution, that the solution containing PO^5 should be used nearly in the same state of concentration as the normal solution of phosphoric acid, and only in quantities of 10—15 cubic centims. In very dilute solutions the phosphate of uranium is deposited more slowly than is the case in very dilute solutions with the phosphate of ammonia and magnesia. The separation of the $(Ur^2O^3)^2\,PO^5$ is more complete when it has the opportunity of taking up NH^3. For this reason ammonia is always added, as well as acetate of soda, in order that no sulphuric or muriatic acid may be set free.—*Journal für Prakt. Chemie.* lxxvi. p. 104.

On the Solubility of Sulphate of Baryta in Nitrate and Muriate of Ammonia. By O. L. Erdmann.

Mittenzwei has remarked that under certain circumstances sulphate of baryta is soluble in considerable quantities in nitrate of ammonia. He has made experiments upon this subject in Erdmann's laboratory by pouring normal solutions of chloride of barium and sulphate of soda alternately into a boiling solution of nitrate of ammonia, which was saturated when cold. In this way no precipitate was produced in 234¾ cubic centims. of fluid which must have contained 0·280 grm. of sulphate of baryta. Precipitation was only effected by an excess of baryta or of sulphuric acid. If the nitrate of ammonia be acidulated with muriatic acid, the solubility becomes still greater. 500 cubic centims. of such a solution, mixed with 50 cubic centims. of muriatic acid held in solution, while boiling, 2 grms. of sulphate of baryta; and even on cooling a considerable portion remains dissolved. In this case the solubility is

occasioned by the presence of free chlorine, for a mixture of 100 cubic centims. of nitrate of ammonia and 100 cubic centims. of muriate of ammonia only retained 0·080 grm. dissolved. According to Erdmann's experiments, $\frac{1}{230000}$th of sulphate of baryta at the utmost remains dissolved in concentrated solution of muriate of ammonia; its separation does not take place immediately; it is more rapid the more dilute the solution, and is complete in 24 hours.—*Journal für Prakt. Chemie*, lxxv. p. 214.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Application to Dyeing of a New Method of Decomposing Hypochlorite of Lime. By M. Sacc.

On issuing from the madder-bath, the stuffs are covered with a stratum of colouring matter which renders the white dingy, and formerly could only be removed by repeated passage through bran or soap-baths, and especially by exposure to the direct rays of the sun on the grass.

When Berthollet discovered the bleaching properties of chlorine, it was supposed that the problem of rapid bleaching was solved, but this hope was soon dispelled in consequence of the difficulty of management and irregularity of action of chlorinated water. Grass bleaching was resumed until Tennant substituted hypochlorite of lime for free chlorine. For many years madder-dyed stuffs have been whitened by passing them into solutions of hypochlorite of lime or soda.

Only a few years ago M. Steinbach thought of printing with a solution of hypochlorite of lime upon the tissues to be whitened, and then drying them upon drums heated by steam, in order to convert the hypochlorite into chlorate and chloride, and thus prevent its ulterior action; in this he was fully successful. This great improvement has, however, the disadvantage that it renders the reds and rose-colours sensibly brown. To avoid this defect, the author has tried the application of hypochlorite of zinc, or rather of its products of decomposition.

By decomposing one equivalent of hypochlorite of lime with a quarter, a half, or a whole equivalent of sulphate of zinc, a liquid is obtained endowed with a more and more energetic bleaching power, and which finally presents all the characters of a solution of pure hypochlorous acid. The stuffs passed into this diluted bath are perfectly bleached without any injury to the red and rose tints; indeed these appear to be rendered more lively. It is unfortunately impossible to print with hypochlorous acid, partly on account of its being rapidly decomposed, and partly because it attacks all organic matters with which it comes in contact.

To ascertain, finally, the non-existence of hypochlorite of zinc, the author tried to substitute salts of zinc for tartaric acid, to obtain whites upon coloured tissues, by passing them into a solution of

hypochlorite of lime. This experiment succeeded to admiration. But this is not all, for by increasing or diminishing the amount of the zinc-salt, the energy of the mordant is increased or diminished to such an extent that by this means we may produce shades as distinct and pure as possible, and such as cannot be obtained by any other process. The following is the mode of operation:—

The following mixture, water 1 litre, gum 500 grms., sulphate of zinc 400 grms., is printed, by the roller, upon the dyed and soaped tissues. When the impression is dry, it is passed for two minutes into a cold bath showing 2° B. with hypochlorite of lime at 100 chlorometric degrees; it is then well washed and dried. This process is far more rapid, sure, and economical than the old one.—*Comptes Rendus*, Feb. 28, 1859, p. 444.

PROCEEDINGS OF SOCIETIES.

Royal Society.

Feb. 24, 1859. (Sir Benjamin C. Brodie, Bart., Pres., in the Chair.)

"Researches on the Phosphorus-Bases."—No. V. Diphosphonium-Compounds. By A. W. Hofmann, LL.D., F.R.S. &c.

In a note* on the deportment of dibromide of ethylene with triethylphosphine, I have stated that the reaction between these two substances gives rise to the production of

Bromide of triethylbromethylene-phosphonium } $[(C_4H_5)_3(C_4H_4Br)P]Br$,

whilst two other bromides, viz.

Bromide of triethylphosphonium $[(C_4H_5)_3HP]Br$ and
Bromide of triethylvinyl-phosphonium } $[(C_4H_5)_3(C_4H_3)P]Br$,

are generated in consequence of secondary processes. But I did not fail to remark in the same note, that in addition there is formed in this reaction a fourth bromide, the nature of which, at that time, I had been unable to fix by experiment.

I have continued the study of this substance, which has led to the following results.

All attempts to eliminate the bromide in question by frequently recrystallizing the direct product of the action of dibromide of ethylene on triethylphosphine have entirely failed. Considerable sacrifice of precious material and often repeated analyses of the different crops of crystallization taught me nothing, except that the body which I endeavoured to grasp is most abundantly produced when the triethylphosphine is rather in excess. Indeed, it would appear, that under those conditions, the bromide in question constitutes the principal product of the reaction.

* Chem. Gaz. vol. xvi. p. 396.

Not more successful was an attempt to increase the chances of separation by reducing the number of the bromides.

As I have previously stated, treatment with oxide of silver destroys the triethylated bromethylene-phosphonium, converting it into a basic compound, which contains no longer any bromine, whilst the same agent transforms the bromide of triethylphosphonium into the oxide of argento-triethylphosphonium, and the dioxide of triethylphosphine. On saturating again by hydrobromic acid the liquid thus produced, the solution now contained only the new bromide, the bromide of the debrominated body, and the dibromide of triethylphosphine, the extreme solubility of which rendered its presence almost harmless. The task was thus virtually reduced to the separation of two bromides. Unfortunately, the two substances resemble each other to such an extent, that this hope also had to be abandoned.

A modification, however, of this process led to the solution of the difficulty. On saturating the alkaline solution, produced by the action of oxide of silver upon the crude bromides, with hydriodic instead of hydrobromic acid, a mixture of the corresponding iodides was obtained, the separation of which could be easily accomplished.

On moderately concentrating this solution, a beautiful iodide of limited solubility was deposited. This substance readily dissolved in boiling water, from which it crystallized on cooling in long white needles. It was less soluble in alcohol, insoluble in ether.

The analysis of this compound, carefully purified by repeated crystallizations, led to the following atomic expression :—

$$C_{14}H_{17}PI.$$

This formula received ample confirmation by the examination of a platinum- and gold-compound. Converted into chloride and precipitated by dichloride of platinum, the new body furnished a crystalline, difficultly-soluble platinum-salt, differing from the platinum-salts of all the other compounds of this group. This salt dissolves in boiling concentrated hydrochloric acid without decomposition, and crystallizes on cooling in beautiful yellow needles containing

$$C_{14}H_{17}PCl,\ PtCl_2.$$

The gold-salt is a bright yellow crystalline precipitate, difficultly soluble in boiling water, and not recrystallizable without some alteration. The gold-determination agreed with the formula

$$C_{14}H_{17}PCl,\ AuCl_3.$$

The preceding formulæ are simple translations of the analytical results, but they convey no idea regarding the nature of the new body. Legitimate interpretation of these expressions, and a due appreciation of the conditions in which the new compounds are formed, unavoidably lead us to the conclusion that the formulæ must be doubled. The molecule of the new iodide thus becomes

$$C_{28}H_{34}P_2I_2,$$

corresponding to an original bromide,

$$C_{28}H_{34}P_2Br_2,$$

which is simply formed by the association of 2 equivalents of triethylphosphine and 1 equivalent of dibromide of ethylene,

$$2C_{12}H_{15}P + C_4H_4Br_2 = C_{28}H_{34}P_2Br_2.$$

The formulæ of the platinum-salt and of the gold-salt of course have likewise to be doubled:

Platinum-salt $C_{28}H_{34}P_2Cl_2$, $2PtCl_2$.
Gold-salt $C_{28}H_{34}P_2Cl_2$, $2AuCl_3$;

the number of platinum- and gold-equivalents which respectively exist in these compounds being apparently determined by the number of triethylphosphine-equivalents associated in the new salt. I have vainly endeavoured to produce compounds containing only one equivalent of platinum and gold, but have succeeded in procuring a well-defined silver-compound:

$$C_{28}H_{34}P_2Br_2,\ AgBr,$$

which is formed by treating the new bromide with a quantity of oxide of silver insufficient for complete decomposition. This compound is a double salt of equal equivalents of the proximate constituents.

The deportment of triethylphosphine with dibromide of ethylene, and more particularly the formation of the new bromide, is not without theoretical interest. The molecule of dibromide of ethylene, equivalent to 2 molecules of hydrobromic acid, fixes in this reaction 2 molecules of triethylphosphine, equivalent to 2 molecules of ammonia, the result being a compound saline molecule, equivalent to 2 molecules of sal-ammoniac.

$$\underbrace{\left[\begin{matrix}H_2\\H_2\\H_2\\H_2\end{matrix}\right\}N_2\Big]Cl_2}_{\text{2 molecules of sal-ammoniac.}} \qquad \underbrace{\left[\begin{matrix}(C_4H_5)_2\\(C_4H_5)_2\\(C_4H_5)_2\\(C_4H_4)''\end{matrix}\right\}P_2\Big]''Br^2}_{\text{Molecule of the diatomic bromide.}}$$

It is not quite easy to frame a name for this complex body, in which, under the influence of the diatomic ethylene, 2 molecules of triethylphosphine are, if I may say so, *dovetailed* together. We have in this case to deal with a compound molecularly representing 2 equivalents of chloride of ammonium, with phosphorus in the place of nitrogen, bromine in the place of chlorine, 6 equivalents of ethyle and 1 equivalent of diatomic ethylene being substituted for the 8 equivalents of hydrogen; in fact, the compound is a dibromide of hexethyl-ethylene-diphosphonium, *sit venia verbo*.

Those who have accorded some attention to the direction of these researches, cannot have failed to observe that the conception of the compound which forms the subject of this note was the point from which I started in examining the deportment of triethylphosphine with dibromide of ethylene. In a note on polyammonias, presented

to the Royal Society about a year ago*, I first pointed out the existence of similar compounds in the nitrogen-series, adducing in favour of this view such experimental evidence as I was enabled to collect from the materials at hand. I have since endeavoured to expand this evidence by the realization of a variety of bodies of analogous constitution. For this purpose I have examined the action of ammonia on dibromide of ethylene; a process, which, owing to the number of bodies simultaneously produced, presents considerable difficulties. With the view of simplifying the reaction, I have passed step by step to the primary, secondary, and tertiary monamines, in which the advancing state of substitution promised a reduction of the number of compounds capable of being generated under the influence of dibromide of ethylene. These experiments, some of which have been laid already before the Royal Society, whilst others are still incomplete, have furnished many additional illustrations of the group of polyammonias; but most of these reactions are complicated, and the compounds produced are far from always presenting the salient characters which I could have desired. In fact, it was not until I pursued the inquiry into the phosphorus-series, and relying on the promptness and precision with which these substances act, examined the deportment of dibromide of ethylene with triethylphosphine, that the experiments were attended with the desired success.

The new diphosphonium-compounds which form the subject of this note are remarkable for their well-defined characters, and for their stability. They may be heated to 250° C. without undergoing the slightest change. Even the dioxide, which is readily liberated by the action of oxide of silver upon either the bromide or the iodide, is a very stable compound. The solution of this substance, which obviously corresponds to 2 molecules of water,

$$\underbrace{\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2}_{\text{2 molecules of water.}} \qquad \underbrace{\left.\begin{matrix}[(C_4H_5)_6(C_4H_4)''P_2]''\\H_2\end{matrix}\right\}O_2}_{\text{Molecule of the diphosphonium-compound.}},$$

is a powerfully alkaline liquid, attracting with great avidity the carbonic acid of the atmosphere, and precipitating the metallic oxides like potassa. The solution may be evaporated without change to a syrup-like liquid, and it is only at a very high temperature that decomposition actually takes place. At one time I had hoped to see this body splitting under the influence of heat into the ethylene-alcohol (glycol) and triethylphosphine, but the transformation ensues in another form, only traces of phosphorus-base being liberated, while the principal product is the dioxide of triethylphosphine, which, in the latter stages of the distillation, coats the neck of the retort with a network of beautiful needles; a small quantity of gas (hydride of ethyle?) being simultaneously evolved.

* Chem. Gaz. vol. xvi. p. 155.

The reaction is probably

$$\left.\begin{matrix}[(C_4H_5)_6(C_4H_4)''P_2]'' \\ H_2\end{matrix}\right\}O_4 = C_4H_6 + 2[(C_4H_5)_3PO_2];$$

this equation, however, is not experimentally established.

The molecule of the diphosphonium-bromide contains the elements of 1 molecule of bromide of triethylphosphonium and 1 molecule of triethyl-vinyl-phosphonium,

$$[(C_4H_5)_6(C_4H_4)''P_2]''Br_2 = [(C_4H_5)_3HP]Br + [(C_4H_5)_3(C_4H_3)P]Br;$$

I have endeavoured to split the latter in accordance with the above equation, but without success.

Triethylphosphine acts with energy upon the homologues of dibromide of ethylene; I have not yet examined, however, any of the products thus obtained. Mr. W. Valentin, to whom I am indebted for much valuable assistance during my experiments, has found, moreover, that triethylarsine unites with dibromide of ethylene. He has not yet completed the investigation of the crystalline body which is generated in this reaction.

March 17, 1859. (Sir Benjamin C. Brodie, Bart., Pres., in the Chair.)

"On the Action of Carbonic Oxide on Sodium-alcohol." By J. A. Wanklyn, Esq.

Dr. Geuther* found that sodium-alcohol $\left(\begin{matrix}C_4H_5 \\ Na\end{matrix}\right\}\right)O_2$, when gently warmed in a stream of carbonic oxide, yielded not propionate of soda, but formiate of soda, with evolution of olefiant gas. The reaction, accordingly, might be represented thus:—

$$\left.\begin{matrix}C_4H_5 \\ Na\end{matrix}\right\}O_2 + C_2O_2 = \left.\begin{matrix}C_2O_2H \\ Na\end{matrix}\right\}O_2 + C_4H_4,$$

and would consist in the replacement of C_4H_4 by C_2O_2.

On inspection of Dr. Geuther's paper it appeared that the above reaction was not established with sufficient certainty. The presence of C_4H_4 as a gaseous product was not satisfactorily proved by direct experiment, but inferred from the production of formiate of soda.

Berthelot has shown that carbonic oxide is capable of uniting with the hydrated alkalies, so as to form alkaline formiates. Also, it is extremely difficult, and perhaps impossible, to obtain sodium-alcohol free from hydrate of soda. It seemed, therefore, not unreasonable to suspect that Dr. Geuther's formiate came from hydrate of soda accompanying the sodium-alcohol employed in his experiments. The investigation about to be described shows that such was really the case.

Sodium-alcohol, freshly prepared from sodium and anhydrous alcohol, was introduced into small glass bulbs, and hermetically sealed therein. One of the bulbs, containing ·406 gramme of

* Annalen der Chem. und Pharm. Jan. 1859.

crystallized sodium-alcohol, was placed in a flask of 155 cubic centimetres' capacity. The neck of the flask was contracted before the blowpipe. Carbonic oxide, after slow passage through potash solution, and then through sulphuric acid, was next made to fill the flask by displacement. Finally, the contracted neck of the flask was closed by fusion, and thus the bulb containing sodium-alcohol was inclosed in an atmosphere of pure oxide of carbon. By agitation the inclosed bulb was broken, and its contents came freely in contact with the carbonic oxide contained in the flask. Particular attention was paid during this stage of the process, and the fused sodium-alcohol was seen flowing over the inner surface of the flask.

After a digestion in the water-bath lasting for more than four hours, the flask was opened under mercury, when a slight contraction was observed in the volume of its gaseous contents. This contraction, amounting to about one-fifth of the entire contents, was due no doubt partly to absorption of carbonic oxide by traces of hydrate of soda, and partly to the difference between the temperature at the time of sealing before the blowpipe, and that at the time of opening under mercury.

The following are the particulars of an examination of the gas contained in the flask after the four hours' digestion at 100° C.

In order to remove any alcohol vapour, the gas was agitated with about one-fifth of its volume of boiled distilled water, when it underwent very little diminution in volume—a circumstance, which shows that no volatile liquid capable of absorption by water had been generated during the reaction.

Some of the washed gas was then treated with a potash bullet and with pyrogallic acid, in order to remove any traces of carbonic acid and oxygen. The amount of these gases present was very trifling, as the readings show:—

Volume of gas taken (corrected (dry) at 0° C. and 1000 millims'. pressure)	65·091
Volume of gas after potash and pyrogallic acid (corrected (dry) at 0° C. and 1000 millims'. pressure)	64·734

After this treatment a portion of the gas was transferred to the eudiometer, in which it furnished the following readings:—

	Volumes.	Temperature. Cent.	Pressure.	Corrected volumes dry at 0° C. and 1000 millims. pressure.
		°	millims.	
Gas taken (moist)	148·0	4·9	202·9	29·500
After the addition of air (moist)	306·5	5·3	352·8	106·077
After explosion (moist)	282·1	5·7	330·6	91·357
After potash (dry)	222·1	5·4	290·0	63·161
After the addition of hydrogen (dry)	294·0	5·7	357·1	102·884
After explosion (dry)	286·4	5·9	350·1	98·150

From which is deduced:—

		In per-centage.
Gas taken	29·500	
Nitrogen	1·072	
Gas free from nitrogen	28·428	100·00
Carbonic acid	28·196	99·18
Contraction	14·720	51·78
Oxygen consumed	14·488	50·96

The theoretical numbers for carbonic oxide and for olefiant gas are as follows:—

	Carbonic oxide.	Olefiant gas.
Volume taken	100	100
Carbonic acid	100	200
Contraction	50	200
Oxygen consumed	50	300

Comparison of the analysis with these numbers will show that the gas was pure oxide of carbon. Furthermore, if we assume that the trifling departure from the theoretical quantities for pure oxide of carbon was due to the presence of olefiant gas, and if we calculate how much olefiant gas would be required, we obtain a negative value for the quantity of olefiant gas from one equation, and a positive one from the other equation, viz.:—

By employing for data the original volume and the carbonic acid generated, the value of $C_4 H_4$ is negative.

$$\text{Vol. of } C_4 H_4 = \text{vol. of } CO_2 - \text{original vol.} = -0{\cdot}82 \text{ per cent.}$$

By employing for data the original volume and the contraction, the value of $C_4 H_4$ becomes positive.

$$\text{Vol. of } C_4 H_4 = \tfrac{2}{3} \text{ contraction} - \tfrac{1}{3} \text{ original vol.} = 1{\cdot}19 \text{ per cent.}$$

This want of conformity shows that $C_4 H_4$ will not satisfy the conditions of the case, and may be regarded as excluding the supposition that a trace even of $C_4 H_4$ was present in the gas examined.

When it is considered that on Dr. Geuther's hypothesis every volume of carbonic acid absorbed should be replaced by an equal volume of olefiant gas, and when it is borne in mind that sodium-alcohol and carbonic oxide must have been less perfectly exposed to mutual action in Dr. Geuther's experiment than in the one just described, I think the conclusion cannot be avoided, that that experimenter's formic acid came not from sodium-alcohol, but from hydrate of soda.

In a previous experiment I failed to obtain propionic acid on exposing at 100° C. carbonic oxide along with sodium-alcohol, and in so far my result agrees with that of Dr. Geuther.

To resume: at 100° C. sodium-alcohol is without action on carbonic oxide.

THE CHEMICAL GAZETTE.

No. CCCCI.—July 1, 1859.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On some Salts of Cerium and Lanthanium. By Dr. Holzmann.

The author has prepared a series of double salts of protoxide of cerium. The material was purified by Bunsen's method; the raw material was Swedish cerite. This was finely powdered, mixed with concentrated sulphuric acid into a thick paste, and evaporated to dryness in the sand-bath; the dry mass was powdered, and extracted several times with boiling water, and finally with dilute nitric acid; sulphuretted hydrogen was passed through the solution, the filtrate boiled and precipitated by oxalic acid after the addition of a large quantity of muriatic acid. The oxalates were washed by decantation with boiling water, then dried, and mixed with an equivalent proportion of calcined magnesia, stirred up with water, dried and exposed to a slight red heat with constant stirring in a porcelain capsule until the oxalic acid was decomposed, and the cerium entirely converted into oxide. This is known by the fact that a sample taken out dissolves in concentrated nitric acid.

The calcined oxides are then dissolved in boiling nitric acid, and the solution heated until nearly all the free acid is expelled; the crystalline mass formed on cooling is dissolved in water. For this purpose each 100 grms. of the salt is triturated in a mortar with 100 cubic centims. of cold water, the solution is rapidly filtered, and put into two litres of boiling water previously mixed with 12 cubic centims. of concentrated sulphuric acid. By this means basic sulphate of cerium separates in a perfectly pure state; it is washed by decantation with the same mixture of water and sulphuric acid.

It is necessary to boil the fluid employed for washing previously to using it, and after the introduction of the precipitate to allow the whole mass to boil up for a short time, as the precipitate then settles more readily, and if this be not done, too large a quantity of it would be dissolved. Basic sulphate of cerium, indeed, exhibits a

very remarkable behaviour. If the nitric solution prepared in the above way be poured into cold water containing the above-mentioned quantity of sulphuric acid, no precipitate is produced by continued boiling, whilst the basic salt thrown down at a boiling heat, when allowed to cool with the fluid, is but sparingly dissolved. Sometimes, even, it appears to lose its slight solubility in water or dilute sulphuric acid entirely, even when it has been always kept moist; for while the supernatant fluid is usually of a yellow colour, it is sometimes colourless, and no trace of cerium can be detected in it. However, even this salt retains its solubility in concentrated acid, which indeed is only lost when it is dried in the air or calcined.

Basic sulphate of cerium may be easily converted into any other compound of cerium, by transforming it by digestion with caustic potash into hydrated protoxide of cerium which is insoluble in concentrated acids.

By boiling with muriatic acid, the latter evolves chlorine and gives protochloride of cerium. It dissolves very readily in dilute acids, when they are mixed with sulphurous acid or some other reducing agent. The solution in nitric acid contains the cerium as protoperoxide.

Double Nitrate of Protoperoxide of Cerium and Potash.—Equal parts of a concentrated solution of nitrate of cerium and of a nearly saturated solution of nitrate of potash, furnish beautiful crystals over chloride of calcium; these resemble bichromate of potash in colour, effloresce quickly when exposed to the air, dissolve very readily in water, become nearly blood-red and decrepitate when heated, and fuse at a higher temperature, at the same time frothing up strongly and emitting red fumes. When ignited in a current of carbonic acid, they leave carbonate of potash and protoxide of cerium.

For analysis an exact determination of the water was made; the bases were then determined in the residue, and the nitric acid calculated from the difference. It gave—

	Found.		Calculated.
	I. and II.	III.	
NO^5	52·799	52·707	52·632
$Ce^3 O^4$	27·794	27·838	27·647
KO	15·222	15·232	16·335
HO	4·185	4·223	4·356
NO^5	55·105	55·031	55·047
$Ce^3 O^4$	29·008	29·065	28·915
KO	15·886	15·904	16·038

from which we obtain the formula

$$\left.\begin{matrix} 2\,KO \\ CeO \end{matrix}\right\} 3\,NO^5 + Ce^2\,O^3, 3\,NO^5 + 3\,Aq.$$

If concentrated solutions of nitrate of cerium and bichromate of potash be mixed in equal proportion, deep yellowish-red crystals separate under the exsiccator after the addition of nitric acid; in

these only nitric acid, potash, and cerium could be detected. From the rapid efflorescence of this salt it could not be analysed; a volumetric analysis showed that the cerium contained in it was in the state of protoperoxide.

Double Nitrate of Cerium and Magnesia.—A yellowish-red salt, rather paler than chromate of potash, which soon becomes opake on exposure to the air, and dissolves readily in water. Its analysis gave—

	Found.		Calculated.
	I.	II.	
NO^5	47·35	47·35	47·76
MgO	6·12	6·23	6·18
Ce^3O^4	25·75	25·47	25·19
HO	20·78	20·95	20·87
NO^5	59·77	59·89	60·65
MgO	7·74	7·88	7·49
Ce^3O^4	32·49	32·23	31·86

This leads to the formula

$$\left.\begin{matrix}2\,MgO\\CeO\end{matrix}\right\}3\,NO^5+Ce^2O^3,3\,NO^5+16\,Aq.$$

Double Nitrate of Cerium and Zinc.—This salt is very similar to the magnesia double salt, but somewhat darker. Analysis:—

	Found.		Calculated.
	I.	II.	
NO^5	43·16	43·16	43·94
ZnO	11·29	11·24	10·99
Ce^3O^4	23·14	23·44	23·09
HO	22·41	22·16	21·98
NO^5	55·62	55·44	56·33
ZnO	14·56	14·44	14·09
Ce^3O^4	29·82	30·12	29·58

from which we obtain the formula

$$\left.\begin{matrix}2\,ZnO\\CeO\end{matrix}\right\}3\,NO^5+Ce^2O^3,3\,NO^5+18\,Aq.$$

Double Nitrate of Protoperoxide of Cerium and Protoxide of Nickel.—This salt is produced by mixing equal parts of concentrated solutions of nitrates of cerium and nickel, and leaving the mixture to stand for some time over chloride of calcium and caustic lime. It forms beautiful, shining, green crystals, often of considerable size, which dissolve readily in water, and soon become moist and dull by exposure to the air.

The analysis of this salt presents extraordinary difficulty, because cerium can hardly be separated from nickel. When the residue from the determination of the water has been ignited until the weight remains constant, it is washed with dilute nitric acid out of the tray into a platinum capsule, evaporated to dryness, and treated with concentrated sulphuric acid; the excess of the latter is then driven off, the residue is dissolved in water, and a little sulphurous

acid, mixed with a great excess of repeatedly crystallized tartaric acid, and neutralized carefully with ammonia, when the nickel is precipitated by sulphuret of ammonium. The smallest excess of sulphuret of ammonium causes the cerium to be thrown down, after the lapse of some time and before the sulphuret of nickel has settled, n a gelatinous form as hydrated protoxide; the whole mass must then be digested for a long time on the water-bath, by which means the cerium is again dissolved, although some nickel is also dissolved with it. When the solution is not very dilute, protosulphate of cerium separates in a crystalline form when it is heated; this only redissolves slowly in a great quantity of water. When the sulphuret of nickel has been separated by filtration, the fluid, which has become slightly acid, is again neutralized, and treated once more as above, adding a few drops of sulphuret of ammonium before bringing the additional precipitate of sulphuret of nickel on a distinct filter. The sulphuret of nickel is dried, dissolved in nitromuriatic acid, the acid neutralized and the solution precipitated while boiling with caustic potash and carbonate of potash; the precipitate is filtered, dried, calcined, and weighed. The fluid filtered from the sulphuret of nickel, which should no longer acquire a brown colour by the addition of ammonia and sulphuret of ammonium, is evaporated to dryness, the tartaric acid destroyed by ignition, and the residue weighed. As a check, this must be again treated with concentrated sulphuric acid, dissolved in water and a little sulphurous acid, and precipitated with oxalate of ammonia; the oxalate of cerium is then separated by filtration, dried, ignited, and weighed. Analyses:—

	Calculated.	Found				
		I.	II.	III.	IV.	V.
NO^5	38·951	38·814	38·768	38·996		
Ce^3O^4	20·460	20·717	20·462	20·417	20·814	20·633
NiO	13·540	13·687	13·975	13·845	13·704	13·770
HO	27·049	26·782	26·795	26·742		
NO^5	53·393	53·012	52·957	53·231		
Ce^3O^4	28·046	28·295	27·951	27·870		
NiO	18·561	18·694	19·092	18·899		

Formula:—

$$\left.\begin{matrix}2\,NiO\\CeO\end{matrix}\right\}3\,NO^5+Ce^2O^3,3\,NO^5+NiO,HO+24\,Aq.$$

The author leaves it undecided whether this is really the formula of the salt; he regards it, however, as not improbable that a portion of the nickel is contained in it as peroxide.

Besides this green double salt, there also exists a brown one, which the author obtained in small quantities by the evaporation of the mother-liquor of the former. A complete analysis of this could not be effected. The salt contains 1 equiv. of protoperoxide of cerium to 1 equiv. of protoxide of nickel.

With other bases the nitrate of protoperoxide of cerium exhibits the following behaviour:—

With *nitrate of soda* it crystallizes with difficulty.

When a moderately concentrated solution of *nitrate of lime* is brought in contact with an equal portion of a concentrated solution of nitrate of cerium, a syrupous yellowish-red mass is gradually formed; this may be drawn out into threads almost like resin, but deposits no crystals even after long standing.

Nitrate of baryta is precipitated, even from rather dilute solutions, by the free nitric acid contained in the solution of cerium.

Pernitrate of iron gives a dark yellowish-red syrupous fluid with nitrate of cerium; this does not crystallize even by standing for weeks over chloride of calcium and caustic lime.

Nitrate of chromium is immediately converted into chromic acid by nitrate of cerium.

Protonitrate of cobalt deposits dark brown hydrated oxide of cobalt when brought in contact with nitrate of cerium; this effect is produced even in the cold, but more rapidly on the application of heat. The fluid, which is at first yellowish red, becomes deep carmine-red. Nitrate of cerium does not throw down any precipitate from a dilute solution of cobalt even when boiled; the fluid, however, acquires a carmine-red colour, which does not disappear on its cooling.

Protonitrate of manganese, whether in a concentrated or dilute solution, whether cold or hot, and even in an acid solution, is precipitated by nitrate of cerium in the form of hydrated peroxide of manganese. This precipitation takes place from the solutions of all protosalts of manganese even when extremely diluted.

Nitrate of lead, in concentrated solution, is also quickly precipitated by the free acid contained in nitrate of cerium.

Nitrate of copper, in concentrated solution, when mixed with a concentrated solution of nitrate of cerium and left for some time over chloride of calcium and caustic lime, crystallizes alone, the cerium remaining in the mother-liquor.

The author also analysed the iodate of the protoxide of cerium. Protonitrate of cerium was put into an excess of aqueous iodic acid, and the salt thrown down washed with hot dilute alcohol, which did not precipitate the iodic acid, and dried on the water-bath. It forms a white, non-crystalline powder, difficult of solution in cold, but more readily soluble in hot water, and very soluble in concentrated and dilute acids.

For analysis, the salt dried at 230° F. was dissolved in hot dilute muriatic acid, the fluid was neutralized and precipitated by oxalate of ammonia, and the oxalate of cerium separated by filtration, dried, calcined, and weighed. The iodic acid was determined in separate portions by volumetric methods. The substance was dissolved in as little hot water as possible, then mixed with some cold water, and treated with iodide of potassium and muriatic acid; the quantity of iodine separated was determined in the ordinary way.

	Calculated.	Found. I.	II.	III.
CeO	24·435	24·610	24·518	24·522
IO^5	75·565	75·390	75·482	75·478

From this the formula would be

$$CeO, IO^5 + HO.$$

On Lanthanium.—As a separation of cerium from lanthanium and didymium is now possible, the author thought that he could also effect a perfect separation of the two latter metals from one another. His experiments have led to the result that we have still no better method than that described by Mosander.

For the preparation of pure lanthanium and didymium, the fluid may be employed which remains in the preparation of pure cerium-compounds after the precipitation of the basic sulphate of cerium. This fluid, together with the washing-water, was evaporated, during which operation a considerable further quantity of cerium separates in the form of basic salt. After this has been removed from the fluid, the latter is evaporated until the greater part of the excess of acid is got rid of. In this operation a large quantity of the sulphates separates in a crystalline form, which only dissolve very gradually in water, but more rapidly on the addition of a little nitric acid; sometimes during cooling a double nitrate of lanthanium, didymium, and magnesia separates in beautiful crystals of an amethyst-red colour. The solution of the crystalline mass and the mother-liquor are precipitated by oxalic acid; the oxalates are again mixed with an equal weight of carbonate of magnesia and exposed for a long time to a dull red heat. The dark brown oxides are then digested with dilute nitric acid, but in such a way that the brown oxide may always be in excess, and the fluid remain neutral. By this means scarcely anything but lanthanium, didymium, and magnesia are dissolved, whilst the cerium remains as basic nitrate in the form of a slightly yellowish, flocculent, voluminous mass. If the filtered fluid be now boiled repeatedly for a long time with carbonate of magnesia, the last traces of cerium separate in the form of basic salt, and only magnesia, lanthanium, and didymium remain in solution; these are precipitated by oxalic acid, the precipitate is dried and calcined, and again dissolved in dilute nitric acid. For the separation of the yttria still contained in it, the solution is mixed with a hot saturated solution of sulphate of potash; the whole mass, in which a few crystalline crusts of sulphate of potash are placed, is left to stand for a few days, the precipitated double salt is washed with a concentrated solution of sulphate of potash, and then digested for a long time with a dilute solution of carbonate of soda. The carbonates thus formed are washed by decantation with boiling water and dissolved in hot dilute sulphuric acid. When the excess of sulphuric acid is expelled, the finely powdered salt is dissolved by constant stirring in six parts of water, whilst the vessel is so cooled from without that the temperature amounts at the utmost to 39° F. The solution is then heated to 95° F., and left at this temperature for some hours,

and then the precipitate formed is washed with water of 95° F. upon a filter, kept at the same temperature. When the mass is kept at this temperature for some time, it appears as if a portion of the sulphate of didymium which is thrown down dissolves again, whilst lanthanium, on the contrary, is still precipitated; by filtration through a cold filter, and washing with cold water, too large a quantity of the precipitate is dissolved. The precipitate is then again dried, and constantly treated as above until pure sulphate of lanthanium is thrown down. As the product becomes richer in lanthanium,the quantity of water must be increased; the temperature during solution must be kept as low as possible, and it must not afterwards be raised to 95° F.; for even when the temperature is gradually raised to 67° F., the lanthanium separates in the form of extremely fine acicular crystals, grouped in tufts, whilst the fluid containing didymium lies above it; but if the solution be heated rapidly to about 95° F., the precipitate is more flocculent, the fluid suddenly becomes converted into a pasty mass, and the precipitate can only be separated with difficulty by washing from the adherent mother-liquor. When the lanthanium is nearly pure, we must employ for the solution of one part of the dry sulphate 9—10 parts of water at 39° F.; but if the mixed salt be under operation for didymium, the quantity of water may be gradually diminished, for a salt which contains much didymium dissolves even in 4—5 parts of water of 39° F., and the precipitation then only takes place at a comparatively high temperature.

In testing whether the lanthanium be really free from didymium, we may easily be deceived. Thus, if the oxalate which still contains traces of didymium be ignited over an ordinary gas-lamp, it appears perfectly white; but if it be heated in an open platinum crucible over a glass-blower's lamp, the white colour is seen gradually to pass into pale brown from the margins inwards, and it is only by continued ignition at so high a temperature that the inner white nucleus, consisting of carbonate and effervescing with acids, disappears.

The author has made determinations of the atomic weight with sulphate and iodate of lanthanium.

Sulphate of Lanthanium, purified, finely powdered, and dried at 212° F., was dissolved in water and precipitated by oxalate of ammonia; the oxalate of lanthanium was separated by filtration, the sulphuric acid in the filtrate was precipitated by chloride of barium, and the sulphate of baryta separated, ignited, extracted with a small quantity of dilute muriatic acid, again dried, calcined, and weighed. The average of three analyses gave as the atomic weight

580·0.

Iodate of Lanthanium was obtained by placing sulphate of lanthanium in aqueous iodic acid, not in a very concentrated state. It is a non-crystalline powder, soluble with difficulty in cold, with more ease in hot water, and dissolving very readily in dilute and concentrated muriatic acid. The average result of the analysis gave the atomic weight =580·2.

Double Nitrate of Lanthanium and Magnesia.—If equivalent proportions of oxide of lanthanium and magnesia be dissolved in dilute nitric acid, without employing an excess of acid, and the mingled solutions be left standing in a cool place over sulphuric acid, very beautifully developed, and often pretty large shining white crystals are formed in course of time; these are readily soluble in water, possess a styptic sweet taste, and only deliquesce after long exposure to moist air. The salt cannot be brought into an anhydrous state without decomposition. As the carbonate remaining in the tray after the determination of the water cannot well be heated before the blowpipe lamp without some loss of the light substance, but only over an ordinary flame, effervescence usually takes place when it is dissolved in nitric acid, and thus from the weights of the separated bases, there appears to be a loss in comparison with the total weight. For this reason two portions of the substance were heated in the same way in platinum crucibles, and calcined before the blowpipe lamp, and then the residue, like that from the determination of the water, was dissolved in nitric acid, and precipitated with oxalate of ammonia; the oxalate of lanthanium was separated by filtration, dried, calcined, and weighed, and the filtrate was evaporated in a platinum capsule, washed and calcined in a platinum crucible, and weighed.

The analysis gave (atomic weight=580·1):—

	Found.					Calculated.
	I.	II.	III.	IV.	V.	
HO	29·64	29·23	29·10	..	..	28·30
NO^5	41·30	41·65	41·95	..	..	42·45
LaO	21·23	21·28	21·14	21·64	21·24	21·39
MgO	7·83	7·84	7·81	7·43	7·85	7·86
NO^5	58·70	58·85	59·17			59·21
LaO	30·17	30·07	29·82			29·82
MgO	11·13	11·08	11·01			10·97

Hence the formula

$$\left.\begin{matrix}MgO\\LaO\end{matrix}\right\} 2NO^5 + 8\,Aq.$$

Journal für Prakt. Chemie, lxxv. p. 321.

On Selenio-cyanide of Allyle. By Professor Wöhler.

It appeared not improbable that there might be a selenio-cyanide of allyle, C^6H^5, NC^2Se^2, analogous to oil of mustard. At the author's request, Tycho Schiellerup made some experiments upon this subject. In the first place, he prepared selenio-cyanide of potassium, and found that this body may be very readily prepared by dissolving selenium in cyanide of potassium. If the cyanide of potassium contains cyanate, the solution need only be boiled in order to destroy this; the selenio-cyanide of potassium may then be separated by alcohol from the carbonate of potash.

A solution of selenio-cyanide of potassium in alcohol was mixed in equivalent weights with iodide of propylene, and distilled on the

water-bath in an apparatus which enabled the product condensed for the first 12 hours to flow back. It was then distilled off and mixed with water. A yellow oil, sinking in water, separated; it had an indescribably disgusting alliaceous odour. In the air, it reddens gradually by the setting free of selenium. When rubbed upon the skin it produces no inflammation.

By treatment with chloride of calcium, this oil became colourless; it boiled between 302° and 363° F., and was evidently a mixture of various bodies. The analysis of the oil, boiling at 302° F., gave 38·5 per cent. of carbon and 42 per cent. of selenium; the formula of selenio-cyanide of allyle requires 32·6 and 54·4 per cent. The material in hand was not sufficient to allow of the further division of the crude product by fractional distillation, and its horrible odour was sufficient to deter any one from further investigations.

By the treatment of the oil with concentrated ammonia, no crystallized product was obtained, although the oil appeared to be somewhat diminished. When the ammonia, which had been in contact with it, was driven off by boiling, and muriatic acid was then added, a quantity of red selenium separated; and when, afterwards, in order to test for a volatile base, solution of potash was added, a further portion of red selenium separated, but dissolved again immediately.

From these experiments it appears, at least, that a selenio-cyanide of allyle, or a similar compound may exist.—Liebig's *Annalen*, cix. p. 125.

On some Reactions of Pentachloride of Phosphorus.
By Dr. R. Weber.

Pentachloride of phosphorus which has been rendered, by the investigations of Cahours and Gerhardt, an important means of preparing many chlorides of the organic radicals, is also capable of decomposing a great number of inorganic compounds and converting them into chlorides.

Very many oxides which occur in nature or are artificially produced, or their compounds, which often obstinately resist the action of very energetic reagents, may be readily decomposed under certain circumstances by pentachloride of phosphorus in such a way as to be converted into chlorides.

This decomposition is effected by passing the vapours of the chloride of phosphorus over the ignited oxide. The simple apparatus required for this purpose consists of a tube of hard glass 7 or 8 inches in length, closed at one end, and bent into an elbow. The open limb of the tube is held in a horizontal position by a suitable wire-clip, and may be heated to any degree by a gas-flame, at the point where the oxide is placed. The chloride of phosphorus is previously placed in the shorter sealed limb of the tube, and by heating it, a tolerably strong current of vapour is produced as soon as the oxide is brought to a red heat. The volatile products of the mutual reaction are for the most part collected in a test-glass.

Silicic acid in the state in which it is obtained in the preparation of fluosilicic acid, or as it is separated in analyses of silicates, was strongly calcined, placed in the tube whilst still hot, and heated to redness. The vapours of chloride of phosphorus were then conducted over it. White clouds were immediately produced, which condensed into a colourless fluid in the receiving glass. In a short time a sufficient quantity of distillate was obtained, whilst the silicic acid visibly diminished. The fluid passing over is usually rendered turbid by a little unaltered pentachloride of phosphorus. When mixed with a little water, it becomes very strongly heated in a few moments; acid vapours escape, and the characteristic jelly of silicic acid is formed, which, when brought in contact with water, does not again dissolve. The author is still occupied with the isolation of the chloride of silicon thus formed.

If, in place of the extremely finely divided silicic acid, powdered quartz be employed, the process is the same, but in consequence of the smaller surface, the decomposition takes place more slowly.

Even at a strong red heat the glass tubes resist the action of the chloride very well, but when the experiment lasts a long time, they are visibly attacked. Then small quantities of chloride of silicon occur amongst the products of distillation, even when bodies have been placed in the tube which contained no silica.

Under similar circumstances volatile chlorides were obained with titanic acid, and these, when carefully put into a large quantity of water, formed a solution of titanic acid, in which a strong precipitate was produced by boiling.

Strongly calcined tin-ashes are quickly decomposed when heated to redness; the volatile chloride betrays itself immediately by a strong vapour which streams out of the tube.

The decomposition of alumina is interesting. Alumina prepared as carefully as possible, and strongly calcined so as to be of a snow-white colour, was treated as above. Close to the red-hot spot there condensed a very slightly volatile compound of chloride of aluminium with chloride of phosphorus. Besides this compound, the unchanged chloride of phosphorus sublimed with the fluid products resulting from its oxidation.

The compound of pentachloride of phosphorus with chloride of aluminium has also been obtained by Dr. Weber by the direct union of the two chlorides. It is nearly white, difficult of fusion, and far less volatile than either of the chlorides by itself. Upon this is founded the process for its separation from the excess of chloride of phosphorus added in its preparation. The fused mass solidifies in a crystalline form on cooling. Its composition was determined by two experiments, which agreed together very well, and led to the formula

$$Al^3 Cl^3 + PCl^5.$$

This compound has much resemblance to the compounds of chloride of aluminium with chloride of selenium and chloride of tellurium.

Even the spathose corundum of Miasc could be decomposed. The crushed mineral was reduced to a fine powder in a steel mortar.

Its decomposition only took place at a strong red heat; but in other respects the phænomena were the same as with alumina.

This process has also been employed with advantage upon native compounds of oxides. Many of the minerals of this kind are only acted upon with difficulty by other reagents, even the strongest.

Titanic iron from Egersund in fine powder is readily decomposed by chloride of phosphorus. If the portion of the glass tube in which the chlorides of titanium, iron, &c. have been deposited be placed in a sufficient quantity of water, a nearly clear solution is obtained, in which a strong precipitate is produced by boiling. Upon this, perhaps, a process might be founded for readily detecting titanic acid in other minerals and precipitates.

The minerals of the spinel group are acted upon more or less readily by pentachloride of phosphorus. Chromic iron from Unst is readily attacked when in fine powder; the volatile chloride of iron escapes in combination with pentachloride of phosphorus.

Franklinite from Sparta in America behaves in the same way.

The fine powder of clear, reddish octahedra of spinel from Ceylon prepared in a steel mortar, was also decomposed when heated to redness by the vapour of pentachloride of phosphorus; the decomposition, indeed, does not take place readily, but still a sufficient quantity of the slightly volatile distillate, containing chloride of aluminium, is soon formed; this dissolves completely in water, and furnishes a copious precipitate with ammonia.

It cannot yet be decided whether the decomposition of chromic iron is complete; the foreign matters contained in the mineral, and the slight volatility of perchloride of chromium, put difficulties in the way of the decision of this question, with the careful investigation of which the author is still occupied.

Simple oxides are decomposed with more facility than these compounds; many of them even exhibit a vivid incandescence when only gently heated in the vapour of chloride of phosphorus.

A straight glass tube 5 or 6 inches long, closed at one end, suffices for these experiments. Some chloride of phosphorus is first of all put into the tube, and upon it the calcined oxide. This is first heated with a small flame, and then the vapours of the chloride are produced. Oxide of cadmium exhibits the incandescence very readily and beautifully, and this is the case to an almost equal extent with calcined oxides of manganese and cobalt.

A peculiarly beautiful light is evolved by magnesia. Even calcined, insoluble oxide of chromium becomes strongly incandescent; violet perchloride sublimes. With oxide of iron, which also becomes incandescent, the perchloride of iron formed escapes in combination with pentachloride of phosphorus.

This compound also has been obtained by the direct combination of the two chlorides; it is of a brown colour, readily fusible, and less volatile than the chlorides alone, a behaviour on which, as with the analogous compound of aluminium, the separation of the excess of pentachloride of phosphorus is founded.

Two concordant analyses of the compound lead to the formula

$$Fe^2 Cl^3 + PCl^5.$$

With less stable oxides the decomposition takes place even at ordinary temperatures.

Here belongs iodic acid. A mixture of arsenious acid with the chloride becomes converted in a short time, without any application of heat, into a colourless liquid, and a great evolution of heat takes place during the reaction. Arsenic acid, when gently heated with the chloride, evolves chlorine. Molybdic acid acquires a brown colour, &c. at ordinary temperatures.

The influence of pentachloride of phosphorus also extends to many salts. Nitrate of silver is decomposed by it, as is also chlorate of potash. At a red heat it also exerts a decomposing action upon wolfram, heavy spar, phosphate of soda, &c.

The experiments relating to the intimate conditions of the decomposition, and also to the products of the decomposition, are not yet completed.

The behaviour of boracic acid, with which he has also occupied himself, has not yet led to any positive result, as the fusibility of boracic acid renders the investigation very difficult.

The causes of the above-mentioned energetic reactions of pentachloride of phosphorus may probably be manifold. In the first place, the predominating affinity of phosphorus for oxygen comes into consideration, and also the great affinity of chlorine for many radicals.

By these oxychloride of phosphorus is produced, and this, at least as far as has yet been ascertained, always occurs amongst the distilled products of decomposition. This body is also formed directly. Bloch found that the vapours of the chloride passed over anhydrous phosphoric acid, were taken up by the latter. He regarded the fluid produced as a compound of equal equivalents of chloride and acid.

The author has found that when anhydrous phosphoric acid and pentachloride of phosphorus are mixed together in the solid state and gently heated, a colourless fluid is obtained, the composition of which from two concordant analyses agrees very accurately with the formula of the oxychloride, $PCl^3 O^2$, established by Wurtz, who obtained this body in a very different, although less direct method, as indeed it may be prepared in various ways. With reference to this, it may perhaps be supposed that in the preparation of the oxychloride by the distillation of chloride of phosphorus with oxalic acid, boracic acid, &c., phosphoric acid is first formed from one part of the chloride of phosphorus by the influence of the water combined with the acid, this then combines with the rest of the chloride in the same way as by the direct employment of anhydrous phosphoric acid. To obtain the oxychloride with the latter, it is as well to employ an excess of it, as the excess of chloride easily becomes mixed with the oxychloride.—*Bericht der Akad. der Wissenschaften zu Berlin*, 1859, p. 229.

On the Determination of Precipitates in Analyses. *By* C. Brunner.

We are indebted to Berzelius for the method now universally adopted of igniting the precipitates with the filter, and determining their quantity by direct weighing and deducting the ashes of the filter. Simple as this process is, two inconveniences sometimes attend it. One of these is the slowness with which complete combustion is often effected, even when the well-known manœuvres are employed; the other relates to the reduction which takes place in some precipitates by the carbon of the filter, when the reduced metal alloys itself in spots with the platinum of the crucible. Thus, if a precipitate of oxide of zinc be ignited with the filter, distinct spots of this alloy may be detected on the crucible. Although these may be of no quantitative importance, and may be easily removed by muriatic acid, it is still desirable to avoid this inconvenience, which may extend to other precipitates.

The following method has long proved the best:—

The vessel in which the precipitates are ignited is a tube of Bohemian glass (such as is employed in elementary analyses), of about 15 centimetres in length and 12 millimetres in diameter. This is drawn out at one end to a rather coarse point, into which a little asbestos is lightly inserted. Thus arranged, it is most accurately tared upon the scales, together with a weight which a little exceeds the weight of the precipitate to be determined. The moderately dry filter is then rolled up with the precipitate, and pushed into the tube, which is then united with the efferent tube of a simple gasometer composed of two glass bottles; the stopcock of the gasometer is then opened, and atmospheric air is allowed to flow through the combustion-tube. The empyreumatic products furnished by the filter, escape in the form of smoke from the point of the combustion-tube; subsequently the filter becomes carbonized, and burns away entirely. Sometimes it is advisable to break up the contents of the tube a little by striking it gently. The combustion always takes place very readily and completely. When the apparatus is cold, the tube is again placed in the scales, and the tared weight is replaced by the necessary weights; thus the amount of the precipitate is determined, and the weight of the ashes of the filter is to be deducted from it.—Dingler's *Polyt. Journal*, cl. p. 374.

On Creatine and Cynuric Acid in the Urine of Dogs.
By Justus von Liebig.

The urine of a dog which had been fed with meat for several weeks, left a mass of crystallized urea when evaporated after being treated with milk of lime. When this was dissolved in alcohol, there remained 50—60 grms. of a snow-white powder, which was soluble in boiling water, and crystallized again from this solution in beautiful glassy crystals. The urine was mixed with milk of lime before evaporation in order to prevent putrescence while it was being collected, and to precipitate the phosphates. The author ascertained

by a special experiment that this creatine may have been produced by the metamorphosis of the creatinine occurring in the urine. Sulphate of creatinine was mixed with milk of lime, the solution was filtered, and left standing for eight months in a closed vessel. After evaporation, an abundance of creatine was obtained, so that there can hardly be any doubt as to the origin of the creatine in the urine of the dog.

In another portion of urine from the same dog, which was mixed with milk of lime and evaporated while quite fresh, only creatinine was found.

When at last the dog was fed with fat alone, and with fat and a little meat, the author found in its urine the cynuric acid formerly described by him, which separated when the evaporated urine was mixed with muriatic acid. The acid separates in short, fine, microscopic needles. When a paste of these fine needles in the fluid in which they were precipitated by nitric acid from their alkaline solution is left standing in a warm place, it loses its voluminous nature, and becomes converted in a few weeks into four-sided, transparent needles of a glassy lustre, often half an inch in length, and of a yellowish colour; when dissolved in alkalies and again precipitated by acids, they recover their original nature and properties. Cynuric acid is an extremely weak acid. Its potash, lime, and baryta salts crystallize readily; the salts have a very alkaline reaction, and are completely precipitated by carbonic acid from their solution in baryta-water in the form of a thick white paste. Two analyses made by Dr. Schindling gave—

Carbon.....	61·81
Nitrogen.....	9·09
Hydrogen	4·59
Oxygen	24·51

The determinations of carbon varied from 61·649 to 61·987; the hydrogen from 4·738 to 4·457; the nitrogen, determined by soda-lime, from 8·769 to 9·418. These numbers approach the formula $C^{16}NH^{7}O^{5}$.

Cynuric acid bears continued boiling with dilute nitric acid; and when heated by itself or with lime, it furnishes an oil with the odour of benzonitrile.—Liebig's *Annalen*, cviii. p. 355.

PROCEEDINGS OF SOCIETIES.

Royal Society.

March 3, 1859.—Sir Benjamin C. Brodie, Bart., Pres., in the Chair.

"Remarks on Organo-Metallic Bodies; 4th Memoir." By Edward Frankland, Ph.D., F.R.S., Lecturer on Chemistry at St. Bartholomew's Hospital.

In a former Memoir* the author described the production of a new series of organic compounds containing the metal tin in com-

* Transactions of the Royal Society for 1852, p. 418.

bination with the radicals methyle, ethyle, and amyle. His attention was at that time especially directed to the compound formed by the union of tin with ethyle, and to which the name stanethyle was given. The iodide of stanethyle was prepared by exposing iodide of ethyle to light or heat in the presence of tinfoil; and, by acting with zinc upon the aqueous solution of this iodide of stanethyle or of the chloride of the same body, stanethyle itself ($C_4 H_5 Sn$) was obtained.

In accordance with a theory of the constitution of all organo-metallic bodies which the author then suggested, the above compounds were respectively represented as the analogues of the proto-iodide and biniodide of tin, thus—

$$\underbrace{Sn\,I}_{\text{Stannous iodide.}} \qquad \underbrace{Sn(C_4H_5)}_{\text{Stannous ethide.}}$$

$$\underbrace{Sn\begin{cases} I \\ I \end{cases}}_{\text{Stannic iodide.}} \qquad \underbrace{Sn\begin{cases} C_4H_5 \\ I \end{cases}}_{\text{Stannic ethiodide.}}$$

It is evident that the application of this theory to the above bodies would receive considerable additional support if the second equivalent of iodine in the stannic iodide could be replaced by ethyle, or some other analogous organic group. In the Memoir already alluded to, it was mentioned, that in studying the behaviour of stanethyle under the influence of heat, evidence was obtained of the existence of this very compound,—stannic ethide, or *binethide of tin*, as it was then named. This body obviously bears the same relation to stannic iodide as stanethyle bears to stannous iodide.

$$\underbrace{Sn\begin{cases} I \\ I \end{cases}}_{\text{Stannic iodide.}} \qquad \underbrace{Sn\begin{cases} C_4H_5 \\ C_4H_5 \end{cases}}_{\text{Stannic ethide.}}$$

Although there could be little doubt of the formation of stannic ethide by heating stanethyle to 150° C., yet the author could not succeed in obtaining the former body in a state of purity from this source: it seemed probable, however, that stannic ethiodide would be easily converted into stannic ethide by bringing it into contact with zincethyle; and a preliminary experiment completely realized this expectation. The results of this reaction, together with its extension to other analogous organo-metallic compounds, form the subject of the present Memoir.

I. *Action of Zincethyle upon Iodide of Stanethyle.*

About two ounces of crystals of iodide of stanethyle were gradually added to a strong solution of zincethyle in ether, care being taken to preserve an excess of zincethyle. On submitting the resulting syrupy liquid to distillation, it began to boil at 70° C.; but the thermometer rapidly rose to 180° C., between which temperature and

200° C. the greater part of the product passed over, solid iodide of zinc containing a little zincethyle being left in the retort. The distillate was washed with dilute acetic acid, and the dense ethereal liquid which separated was dried over chloride of calcium, and rectified. The greater portion of it distilled at 181°, and was collected apart. Submitted to analysis, it yielded results leading to the formula—

$$Sn \left\{ \begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix} \right.$$

The following equation, therefore, expresses the action of zincethyle upon iodide of stanethyle:—

$$\left. \begin{matrix} Sn(C_4H_5)I \\ Zn(C_4H_5) \end{matrix} \right\} = \left\{ \begin{matrix} Sn(C_4H_5)_2 \\ ZnI \end{matrix} \right.$$

Stannic ethide or binethide of tin is a limpid colourless liquid even at −13° C., possessing a very faint ethereal odour, resembling that of oxide of stanethyle, and a slightly metallic, though not unpleasant taste. Its specific gravity is 1·187 at 23° C. A determination of the specific gravity of its vapour gave the number 8·021, showing that stannic ethide consists of one volume of thin vapour and four volumes of ethyle, the five volumes being condensed to two. Stannic ethide boils at 181° C., and distils unchanged, thus differing from stannous ethide, which decomposes at 150°, chiefly into metallic tin and stannic ethide, a reaction calling to mind the behaviour of stannous oxide when boiled with a caustic alkali. Stannic ethide is inflammable, burning with a lurid flame fringed with deep blue and evolving white fumes of stannic oxide. In oxygen it burns much more brilliantly, with a white light fringed with blue.

It was important to ascertain the deportment of stannic ethide with negative elements, since, if it were found to be capable of direct combination, its analogy to inorganic stannic compounds would be, to a great extent, disproved. Like zincethyle, however, stannic ethide is incapable of combining with any other element without the expulsion of at least an equivalent amount of its ethyle. Treated with iodine, the latter dissolves with a deep brown colour, which, however, gradually disappears; and if the addition of iodine be continued until decolorization be no longer effected, the resulting liquid, on being submitted to distillation, is found to consist of iodide of ethyle, which distils over, and an iodine salt, possessing the unbearably pungent odour of one of the products of the action of tin upon iodide of ethyle at 160° C., and described by MM. Cahours and Riche as iodide of distannous ethyle, $Sn_2(C_4H_5)_2I$. The iodine salt appears, in fact, to be either identical with this body or to consist of *stannic iodotriethide* ($Sn_2(C_4H_5)_3I$)*.

* Whilst I was engaged with these experiments, Mr. Buckton announced the formation of stannic ethide (Chemical Gazette, vol. xvi. p. 419), and mentioned his intention to study the salts formed by the action of iodine, bromine, &c., upon that body; I have not, therefore, prosecuted the inquiry further in this direction.

Stannic ethide does not decompose water, and is not acted upon by strong aqueous hydrochloric acid in the cold. When, however, heat is applied to the mixture of the two liquids, bubbles of gas are slowly evolved; but it requires from twelve to eighteen hours to complete the reaction. The gas was found to be pure hydride of ethyle, and the quantity evolved was such as to show that exactly one equivalent of ethyle was expelled in the form of hydride from two equivalents of stannic ethide, indicating the following reaction:—

$$\left.\begin{matrix} 2\,Sn(C_4H_5)_2 \\ HCl \end{matrix}\right\} = \left\{\begin{matrix} C_4H_5H \\ Sn_2(C_4H_5)_3Cl. \end{matrix}\right.$$

II. *Action of Zincmethyle upon Iodide of Stanethyle.*

About three ounces of crystallized iodide of stanethyle were gradually added to a solution of zincmethyle in ether. Considerable heat was evolved, and the vessel in which the reaction was performed required to be plunged into cold water. On treating the product as before described, a liquid was obtained boiling between 143° and 148° C., and yielding, on analysis, numbers closely corresponding with the formula

$$Sn\left\{\begin{matrix} C_4H_5 \\ C_2H_3. \end{matrix}\right.$$

The action of zincmethyle upon iodide of stanethyle may therefore be thus expressed:—

$$\left.\begin{matrix} Sn\left\{\begin{matrix} C_4H_5 \\ I \end{matrix}\right. \\ Zn\,C_2H_3 \end{matrix}\right\} = \left\{\begin{matrix} Sn\left\{\begin{matrix} C_4H_5 \\ C_2H_3 \end{matrix}\right. \\ Zn\,I. \end{matrix}\right.$$

The new body thus formed, and for which I propose the name *stannic ethylomethide*, is a colourless limpid liquid, undistinguishable in appearance from stannic ethide. It possesses, like the latter, a very faint ethereal odour and a slightly metallic taste. Its specific gravity is 1·2319 at 19° C. It does not solidify at −13° C. Stannic ethylomethide boils between 144° and 146° C. The specific gravity of its vapour is 6·838, showing that its constitution is similar to that of stannic ethide. It is easily inflammable, and exhibits the same deportment as stannic ethide with chlorine, iodine, and bromine; its combination with these elements being always attended with the expulsion of methyle. Stannic ethylomethide dissolves iodine, assuming a magnificent crimson colour, which disappears with extreme slowness unless heat be applied. When, however, action has once been set up, it goes on with considerable rapidity, even in the cold. The products of this reaction were proved to be iodide of methyle and iodide of distanethyle:—

$$2\left\{\begin{matrix} C_4H_5 \\ C_2H_3 \\ 3I \end{matrix}\right\} = \left\{\begin{matrix} 2C_2H_3I \\ Sn\left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ I. \end{matrix}\right. \end{matrix}\right.$$

Iodide of distanethyle, which has already been partially examined, although with discordant results, by M. Löwig and by MM. Cahours and Riche, is a dark straw-coloured, somewhat oily liquid, which does not solidify at −13° C. It possesses an extremely pungent and intolerable odour, resembling oil of mustard. Its specific gravity at 15° C. is 2·0329. At 208° C. it enters into ebullition, but cannot be distilled without decomposition.

Treated with hot hydrochloric acid, stannic ethylomethide is decomposed, yielding a crystallizable salt and a gaseous mixture, consisting of—

Hydride of ethyle	81·21
Hydride of methyle.....	18·79
	100·00

III. *Action of Zincethyle upon Iodide of Mercurymethyle.*

The formation of stannic ethylomethide in the manner just described, encouraged the author to attempt a similar reaction with iodide of mercurymethyle, $Hg \left\{ \begin{matrix} C_2H_3 \\ I \end{matrix} \right.$. Mr. Buckton's announcement* of the formation of mercuric ethide, $Hg \left\{ \begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix} \right.$, by an analogous reaction, tended also to strengthen the hope that a mercuric ethylomethide might be thus obtained.

Iodide of mercurymethyle is readily acted upon by zincethyle, but no mercuric ethide was produced, the reaction being expressed by the following equation:—

$$\left.\begin{matrix} Hg\,(C_2H_3)\,I \\ 2Zn\,(C_4H_5) \end{matrix}\right\} = \left\{\begin{matrix} Hg\,(C_4H_5)_2 \\ Zn\,(C_2H_3) \\ Zn\,I. \end{matrix}\right.$$

IV. *Action of Zincmethyle upon Chloride of Mercuryethyle.*

Although the above reaction failed to produce mercuric ethylomethide, it was still possible that this body might be formed by acting upon a mercuryethyle compound with zincmethyle. About five ounces of chloride of mercurous ethyle ($Hg\,(C_2H_5)\,Cl$) were added to four ounces of a strong ethereal solution of zincmethyle. Considerable heat was evolved; and after forty-eight hours the product was distilled. All the volatile portion came over below 140° C. The distillate was washed with weak acetic acid, dried over chloride of calcium, and then rectified. A considerable portion distilled between 127° and 137° C., and was collected apart. The last few drops came over at 156° C. Repeated rectifications of the product boiling between 127° and 137° C. did not serve to isolate any portion of the distillate, having a fixed boiling-point; on the contrary, in was evident that the range of the temperature of distillation became

* Chem. Gaz. vol. xvi. p. 416.

wider each time the operation was repeated. A section boiling between 127° and 133° gave, on analysis, 13·68 per cent. of carbon, whilst another section, boiling between 141° and 143°, gave 16·71. The formula $Hg \left\{ \begin{matrix} C_4 H_5 \\ C_2 H_3 \end{matrix} \right.$ requires 14·75 per cent. of carbon. Mercuric methide boils at 96°, and mercuric ethide at 159° C.; consequently mercuric ethylomethide might be expected to boil at about 128°. The author considers it more than probable that mercuric ethylomethide was formed in the above reaction; but subsequent distillations gradually transformed it, more or less perfectly, into a mixture of mercuric ethide and mercuric methide.

$$2\,Hg \left\{ \begin{matrix} C_4 H_5 \\ C_2 H_3 \end{matrix} \right\} = \left\{ \begin{matrix} Hg\,(C_4 H_5)_2 \\ Hg\,(C_2 H_3)_2. \end{matrix} \right.$$

V. *Action of Zinc upon a Mixture of the Iodides of Ethyle and Methyle.*

In a former memoir* the author pointed out that the vapour volume of zincethyle indicated the constitution of that body to be represented by the formula $\left. \begin{matrix} C_4 H_5 \\ C_4 H_5 \end{matrix} \right\} Zn_2$; but it is evident that this formula would receive important confirmation if the double equivalent of zinc could be made to combine with two radicals of different composition. An attempt was made to produce such a body by submitting simultaneously the iodides of methyle and ethyle, mixed with an equal volume of ether, to the action of zinc at 100° C. In eighteen hours the decomposition of the iodides was complete, and the distilled product, on being rectified, began to boil at 38°, ether and zincmethyle distilling over; the thermometer then gradually and uniformly rose to 120° C., at which temperature the remainder of the product, consisting of pure zincethyle in considerable quantity, distilled over. No evidence whatever was obtained of the existence of an intermediate compound containing both ethyle and methyle.

VI. *Zincmethyle.*

The experiments detailed in the foregoing pages requiring the use of considerable quantities of zincmethyle, the author's attention was directed to the preparation of this body in much larger quantities than could be obtained by the operations in sealed glass tubes previously described by him. He found that the preparation of a strong ethereal solution of zincmethyle succeeded most satisfactorily in a copper digester, heated to 100° C.; in fact, the decomposition by zinc of an ethereal solution of iodide of methyle is much more quickly and perfectly effected than that of a similar solution of iodide of ethyle; but on submitting the product to rectification, a liquid was obtained boiling at about 51° C., spontaneously inflammable to the last degree, and possessing the intolerable odour of zincmethyle. On analysis, however, it yielded numbers closely agreeing with the

* Transactions of the Royal Society for 1855, p. 266.

formula—

$$2\left(\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right\}Zn_2\Big)+\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2.$$

The specific gravity of its vapour was 3·1215, a number which does not correspond with the theoretical specific gravity of a *compound* of the above formula, unless the exceedingly improbable assumption be adopted, that it contains two volumes of zincmethyle vapour, united with one volume of ether vapour, *without* condensation. On the other hand, it accords closely with the specific gravity of the vapour of a *mixture* of zincmethyle and ether in the above proportions.

Without at present offering any decided opinion as to the nature of this body, the author states that in repeated operations with large quantities of materials he has entirely failed in obtaining *pure* zincmethyle by this method of proceeding.

Similar repeated attempts to produce pure zincethyle from zinc and iodide of methyle, without the intervention of ether, were also unsuccessful, although this method generally succeeds in small glass tubes. This anomaly in the results obtained from the same materials heated in a copper digester and in glass tubes, is doubtless due to the difference of the conditions in the two cases. In a glass tube half immersed in a heated oil bath, a constant distillation of the internal liquid is going on, the liquid condensed in the upper portion of the tube flowing over an extensive surface of zinc in its descent; whilst, in a digester of thick copper, the different parts of the vessel, owing to the high conductivity of the metal, are maintained at so uniform a temperature as to prevent any such circulation of the liquid from taking place.

The body just described being regarded as a mere mixture of zincmethyle and ether, incapable of being separated on account of the close proximity of their boiling-points, a more successful result was anticipated by mixing the iodide of methyle with methylic ether instead of vinic ether. As methylic ether boils at −21° C., it was thought that no such difficulty of separation could arise; the bodies employed would then, in fact, be exactly homologous with those so successfully used in the preparation of pure zincethyle on the large scale. It was found, however, that although a large quantity of zincmethyle was produced, yet it was impossible to obtain it free from methylic ether. A large portion of the product boiled at 43°, a small residuum only distilling between this temperature and 48°; both portions yielded, on analysis, results approaching the formula

$$2\left(\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right\}Zn_2\Big)+\left.\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right\}O_2.$$

This result is, therefore, homologous with that obtained by the decomposition of iodide of methyle mixed with vinic ether.

In conclusion, the author states, that after an expenditure of many pounds of iodide of methyle, he has been unable to obtain even the smallest quantity of pure zincmethyle by the use of a copper digester, although a much larger product of the ethereal solution is obtained than in the corresponding preparation of zincethyle.

THE CHEMICAL GAZETTE.

No. CCCCII.—July 15, 1859.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Coal-gas upon various Saline Solutions, especially on an Ammoniacal Solution of Protochloride of Copper. *By* Professor Rudolf Böttger.

As early as 1852 the author commenced experiments upon the behaviour of ordinary lighting gas (prepared from coal or resin, or from a mixture of Boghead coal and resinous wood) to various saline solutions and fluids. For the removal of various impurities which weakened the illuminating power of the gas, the author employed amongst others the absorbent so highly extolled by Leblanc for carbonic oxide gas, namely an ammoniacal solution of protochloride of copper. Leblanc states (and his statement is confirmed by Dr. Vogel, jun.) that when a current of carbonic oxide gas is passed through a solution of protochloride of copper in muriatic acid or in caustic ammonia, the gas is absorbed with as much rapidity as carbonic acid by caustic potash, and that this furnishes a new analytical means for separating carbonic oxide with facility from gaseous mixtures. The author found, however, that the solution of carbonic oxide gas in this fluid takes place with extreme slowness.

If a very slow current of carbonic oxide (obtained by heating crystallized oxalic acid in concentrated sulphuric acid), completely freed from carbonic acid by means of solution of potash, be passed through three Liebig's bulb-tubes placed one behind the other, and filled with ammoniacal solution of protochloride of copper, neither turbidity nor precipitate is seen to be produced in the solution, however long the passage of the stream of gas may be continued, and the gas flowing out from the last bulb-tube burns, when a flame is brought near it, with its peculiar beautiful blue flame just as quietly and continuously as if it had passed through no absorbent agent. Now

as an ammoniacal solution of protochloride of copper is decomposed in a far higher degree by a carburet of hydrogen contained in lighting gas, the above-mentioned saline solution can by no means deserve the importance as an absorbent for carbonic oxide gas, which has been attributed to it by Leblanc and Vogel.

Indeed it appears remarkable that Leblanc, who, in conjunction with Stas and Doyère, made use of the ammoniacal solution of protochloride of copper as an absorbent for carbonic oxide in an illuminating gas, should have overlooked, or passed without notice, phænomena and reactions which under these circumstances infallibly make their appearance in a striking degree in the course of a few minutes. Indeed, these remarkable phænomena, which occur during the action of coal-gas upon an ammoniacal solution of protochloride of copper, are not referred to anywhere in the literature of chemistry.

If ordinary coal-gas, before it is allowed to flow into the Bunsen's gas-lamp, which is now almost universally introduced into the laboratories, be passed through a Woulfe's bottle of about 12—16 cubic inches capacity and two-thirds full of ammoniacal solution of protochloride of copper, by allowing it to enter through a glass tube, fastened in a perforated cork, and opening a few lines below the surface of the fluid, whilst it escapes through a second elbowed tube, terminating just below the cork of the bottle, and communicating by a caoutchouc tube with the gas-lamp, the upper part of the inner wall of the bottle is covered with a coating of a nearly cinnabar-red colour in the course of a few minutes, and by degrees the blue fluid also becomes filled with cinnabar-red flakes, which accumulate to such an extent in the course of a few hours, that they not unfrequently occupy the whole lower fourth of the bottle. By the employment of such a washing-bottle, which may be filled with the most different saline solutions, we obtain a simple arrangement, by which, without any particular expenditure of gas, the most multifarious experiments of absorption with combustible gases of all kinds may be effected, as the gas-lamp may be employed at the same time as usual in heating and evaporating fluids, &c.

As no visible alteration is produced in the ammoniacal solution of protochloride of copper by the passage of carbonic oxide, carbonic acid or pure hydrogen gas, and, as we shall see hereafter, the above red flocculent body is in all probability a compound of copper and a carburet of hydrogen, it was easy to suppose that either pit gas ($C^2 H^4$), which is contained in considerable amount in coal-gas, or elayle gas ($C^4 H^4$) might cause the production of this cinnabar-red body. Direct experiments made with these gases gave, however, an unmistakeably negative result. By agitating benzole ($C^{12} H^6$) and crystallized naphthaline ($C^{20} H^8$) with the ammoniacal solution also, the author was unable to produce the red body. It therefore only remained to bring the ammoniacal solution of protochloride of copper in contact with the higher hydrocarbons which not unfrequently occur in variable quantities in coal-gas, especially with propylene ($C^6 H^6$), butylene ($C^8 H^8$), and amylene

($C^{10}H^{10}$). The gaseous mixture produced by the dry distillation of equal weights of anhydrous acetate of soda and soda-lime, which, as is well known, contains all the last-mentioned hydrocarbons, was found to have no action upon the ammoniacal solution of copper.

But the knowledge of the hydrocarbon which is combined with copper in this remarkable body, can only be attained with certainty when a process has been found for its production in a state of purity sufficient for a quantitative analysis. If we attempt to wash it upon a filter, first with caustic ammonia and then with alcohol, its great instability is soon seen from the change in its colour, which passes, especially while it is being dried, from cinnabar-red to brownish violet. It appears, however, from the qualitative analytical experiments already made, that we have to do in this case with a body of very unusual composition, in which the hydrocarbon acts towards the copper as a compound radical, in the same way as cyanogen. Analogous compounds are producible also with gold and silver.

If a current of coal-gas be passed continuously through a solution of protochloride of copper in muriatic acid, no change is perceived in the latter, but, on the contrary, the red body is soon formed by the same treatment in an ammoniacal solution of the canary-yellow hyposulphite of protoxide of copper and soda (obtained by precipitating a solution of sulphate of copper with hyposulphite of soda), and also in the ammoniacal solution of the orange-coloured sulphite of protoperoxide of copper (obtained by heating a solution of sulphate of copper with sulphite of soda).

The properties of the red compound are as follow:—

In the moist state the body appears flocculent, not crystalline, nearly cinnabar-red; in the dry state it appears brown with a tinge of violet. When laid quite dry between bibulous paper and struck moderately hard with an iron hammer upon an iron anvil, it is decomposed with a hissing sound and scattering of sparks, and leaves behind a great quantity of a satin-black, uncommonly voluminous powder (consisting of finely divided carbon and metallic copper). When heated in a thin-walled test-glass, it is decomposed between 246° and 302° F., whether suddenly or gradually heated; it detonates strongly, and leaves behind a black powder (a mixture of carbon and copper), amounting to at least three times its original volume. In a moist state it is dissolved without decomposition, that is without evolution of gas, when agitated with very dilute muriatic acid at a moderate temperature; it then forms a greenish-yellow fluid, which may be mixed with any quantity of water without alteration, and from which, by imperfect neutralization with caustic potash, the body may be precipitated with its original red colour, and all its original properties. If, on the other hand, it be treated in the moist state at a moderate temperature with muriatic acid of spec. grav. 1·1, it dissolves partially with a scarcely perceptible and very brief evolution of gas, but on the application of heat complete solution takes place, with a very tumultuous evolution of gas; the gas set free is inflammable and burns, when a taper is brought close to it, with a flame of an intense yellowish-white colour, and a simul-

taneous deposition of soot. The fluid produced by this process and thus deprived of its gas, consists simply of protochloride of copper containing muriatic acid, from which caustic potash precipitates yellow hydrated protoxide of copper. Acetic acid, dilute sulphuric acid, and solutions of potash, soda, and ammonia do not attack the body even when heated; on the other hand, it is dissolved even at a moderate temperature by a concentrated solution of cyanide of potassium, when carburetted hydrogen gas is evolved and a colourless fluid is formed, from which, when evaporated, readily soluble protocyanide of potassium and copper may be obtained in crystals. If a little of the perfectly dry substance be thrown into a bottle filled with chlorine gas, a slight detonation takes place instantly with evolution of light; chloride of copper and muriatic acid are formed, and finely divided carbon is deposited. If a little of the dry powder be loosely rolled up in one end of a long strip of bibulous paper, and let down into an atmosphere of chlorine, a very slight and quite innocuous detonation takes place instantly, whilst on opening the paper, which is not unfrequently quite uninjured, a quantity of very voluminous carbon is found. When the powder, loosely rolled up in bibulous paper, is immersed in an atmosphere of vapour of bromine, ignition and, of course, decomposition takes place, with separation of finely divided carbon. If nearly equal volumes of the dry explosive powder, and finely powdered iodine be mixed together with avoidance of any friction, the mixture becomes ignited in the course of a few moments, with a hissing noise, and leaves behind finely divided carbon. If it be intimately mixed with an equal volume of chlorite of lead, a very slight friction suffices to cause it to explode. If the explosive body, when dried under a bell-glass over sulphuric acid, has become a little oxidized, it no longer exhibits the property of becoming decomposed spontaneously when mixed with powdered iodine; but to render it capable of this, it need only be digested a few times with liquid ammonia, then washed with alcohol, and dried in an atmosphere of hydrogen.

From the reactions here adduced, we are justified in regarding the explosive body under consideration as a carbohydruret of copper, which might be arranged in some respects with the hydruret of copper obtained by Wurtz by the mutual action of solution of sulphate of copper and hypophosphorous acid, and also with that obtained by Poggendorff at the negative pole in the decomposition of a slightly acidulated and sufficiently dilute solution of sulphate of copper by means of a tolerably strong galvanic current.

As regards the action of coal-gas upon certain solutions of gold and silver, the author has as yet only made a few experiments upon this point.

If ordinary lighting gas be conducted continuously through a solution of nitrate of silver and ammonia with an excess of ammonia, the solution becomes slightly reddened in the course of a few minutes, and by degrees an extremely fine, blackish-grey, flocculent

(not crystalline) body is seen to separate in it, the colour of which gradually becomes darker, and at last quite black. When perfectly dry, this body exhibits the following properties:—At a moderate temperature it is not perceptibly acted upon or changed by nitric acid of spec. grav. 1·3. It explodes both by a blow from iron upon iron and by an elevation of temperature, with far more violence than the above-mentioned copper compound. If it be decomposed in very small quantities by heating in a rather long test-glass, an extremely light, very voluminous, deep black powder is seen to be produced after each detonation; this consists of finely divided carbon and metallic silver, and when heated upon platinum-foil, with access of air, smoulders away, and leaves metallic silver. If as much of it as can be taken up on the point of a small knife be thrown into a vessel filled with chlorine, a strong but perfectly harmless detonation takes place immediately, with deposition of chloride of silver and of an uncommonly voluminous, deep black carbon. On mixing nearly equal volumes of this body and finely powdered iodine, a detonation takes place almost instantly and without the least friction; a large quantity of finely divided carbon is again deposited. A mixture of equal volumes of this explosive compound and chlorite of lead detonates with the most fearful report on the application of the slightest friction.

When coal-gas is passed through an ammoniacal solution of freshly precipitated chloride of silver, the explosive, black silver compound is not obtained. The crystalline precipitate, of a greyish-white aspect, recently obtained by Professor Vogel by passing coal-gas through a solution of nitrate of silver, which explodes with great violence both when heated and also, according to the author's observations, when put into an atmosphere of chlorine, appears to be distinct from the flocculent, black body here referred to.

By passing coal-gas, washed (*i. e.* freed from ammonia) by means of dilute sulphuric acid, for several hours through a solution of chloride of gold, as free from acid as possible, a brownish precipitate is gradually formed, which, when well washed and dried, explodes with extreme violence on the application of heat. The glass in which the decomposition of the solution of gold takes place, usually becomes coated on the inside with a very thin, firmly adherent and extremely brilliant film of gold.

If coal-gas be passed through a solution of protoxide of copper in ammonia, a copper compound is thrown down, which from the moment of its production forms a dark violet, flocculent precipitate; this only needs to be washed with water in order to obtain it in sufficient purity. Its external appearance does not change essentially during desiccation, and it appears to possess explosive properties in a still stronger degree than the compound prepared from protochloride of copper. The blue fluid which is obtained by the continued agitation of copper-scale with strong ammonia, consists almost entirely of protoxide of copper and ammonia, with an extremely small intermixture of peroxide of copper and ammonia; on the passage of coal-gas it loses its colour completely in a very short

time, and if the passage of the gas be still continued, a considerable quantity of this interesting body is soon obtained.—Dingler's *Polytechn. Journal*, clii. p. 22.

On the Organic Substance in the Meteoric Stone of Kaba. *By* Professor Wöhler.

The following note on the organic matter contained in the meteoric stone of Kaba was communicated by Haidinger to the Academy of Sciences at Vienna.

Experiments made with about 10 grms. of powder and small fragments of the meteoric stone of Kaba, have shown that this meteorite, beside its free carbon, contains a carburetted substance, which appears to have some similarity with certain fossil carburets of hydrogen, such as the so-called mineral tallows, Ozokerite, Schererite, &c., and is undoubtedly of organic origin. Perhaps it is only a small residue of a larger quantity which the meteorite previously contained, and which was destroyed at the moment of the fiery phænomenon with deposition of carbon.

The fragments were reduced to powder, extracted with perfectly pure alcohol, which was then filtered and evaporated. There remained a colourless, white, apparently crystalline mass, which possessed a weak, peculiar aromatic odour. It was soluble in alcohol, and this solution was rendered milky by the addition of water. In æther it was broken up into small oily drops, as if it had been decomposed into an insoluble, fluid, and a soluble solid portion. On the evaporation of the æther, the latter remained in a distinctly crystalline form. When heated in the air, the substance was volatilized in white fumes of a slightly aromatic odour. When, on the contrary, it was heated in a narrow tube, it fused very readily, and was decomposed by a stronger heat, with deposition of a black coal and evolution of a fatty odour. The substance remained unaltered in caustic soda.

The pulverized stone, which had been treated with alcohol, when ignited in oxygen gas, gave but little vapour, and only a trace of sublimate, but a large drop of water, although it had been carefully dried beforehand. The powder, which had acquired a cinnamon-brown colour, became heated when water was poured over it; for it contained a large quantity of sulphate of magnesia, extractible by water, and some sulphate of nickel, formed by the sulphur of the sulphuret of iron contained in the stone.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xxxiv. p. 7.

On the Relations of the Soil to Vegetation. *By* M. Boussingault.

From an investigation of the conditions of fertility of the soil Boussingault draws the following conclusions:—

1. That in an extremely fertile soil the amount of nitrogen, although derived from organic matters, and in part still combined in them, cannot be the cause of fertility.

2. That the nitrates and ammoniacal salts are the only compounds which convey assimilable nitrogen to the plant, whether these salts pre-exist in the soil, or are only formed during the progress of cultivation.

3. That a plant, in order to be capable of its normal development, must have a very great volume of earth at its disposal, because the amounts of nitric acid and ammonia, which are contained in a given volume of soil, are very small.

4. That the analysis of a soil as to its amount of nitrogen cannot serve as the foundation of any opinion as to its fertility, because it gives the amounts in an assimilable and unassimilable form together.

5. That when the soil is lying fallow, a considerable quantity of the carbon of the organic matters which it contains is lost, but that the amount of nitrogen does not diminish but increases. Whence this increase arises, whether it is caused by nitrification, or by the production or absorption of ammonia, is still to be ascertained.—*Comptes Rendus*, xlviii. p. 307.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Chinese Green (Vert de Chine *or* Lo-kao).

A VERY valuable contribution to scientific literature has been furnished by the Chamber of Commerce of Lyons in the form of a memoir of 207 pages, prepared at their request by 1. Natalis Rondot, who reports upon the origin of the above colouring matter and its mode of manufacture and employment in China; 2. Professor J. Persoz, who furnishes the investigation of its chemical properties and its behaviour towards spun fibres; and 3. A. F. Michel of Lyons, who communicates his experiments with indigenous colouring matters capable of replacing the Chinese green.

In the following abstract the historical notice of the Chinese green, as well as the references to other yellow, blue, and green dyes made use of in China, are passed over.

From the report of Rondot, which goes very much into detail, it appears that for the knowledge of the genera and species of plants from which the Chinese green is extracted, we are indebted to the French Consul at Shanghai, De Montigny, and to Professor Decaisne of Paris, and it is to be regarded as indubitable that this colouring matter is furnished by species of *Rhamnus*. Decaisne describes two species in particular which are brought from China to Europe. In China these plants are called Lo-chou; Decaisne names one of them *Rhamnus utilis*, the other *R. chlorophorus*. The most different organs of these plants appear to furnish the Chinese green; at least this is certainly asserted of the bark of the twigs and that of the roots; and the flowers are also said to contain this colouring matter; but with regard to the berries the reports are

contradictory, some reporters stating that they are of no use, whilst others consider the Lo-kao to be prepared from them. In China the wood of the branches, as well as their bark, is an article of commerce. The price of the double hundred-weight of the former is 6—9 francs at different markets, that of the latter 11—50 francs, according as the substances are yielded by one or other of the plants. The Lo-kao, which may be regarded provisionally as a lake, which is obtained from the above-mentioned species of *Rhamnus*, has been purchased on the spot by various French and English merchants at prices varying between 224 and 430 francs per kilogramme. At Lyons its highest price has been 750 francs, and its lowest 250 francs, the average being 400—500 francs per kilogramme. According to various reports, these substances are employed in China in the following way:—

a. *Cotton dyeing.*—According to one reporter, the bark is extracted with hot water, and the stuffs dyed in the extract without any mordant. The dyed stuffs are laid over-night upon the turf, and towards morning, before the sun has shone upon them, the upper side has acquired the green colour. According to the second report, by the Jesuit Father Helot, the cotton-dyeing is effected in the following manner in Azé:—The fresh bark of *Rhamnus utilis* is extracted with hot water, and the fluid left standing upon the bark for two days. The bark of *R. chlorophorus* is treated in the same way, but left standing for ten days. The stuffs are then dipped into the first decoction seven times, into the second three times, allowing them to dry after each passage; in the evening they are spread upon the turf, and left until sunrise, when the upper side alone appears of a green colour. In another place, according to the same reporter, the decoction is prepared by means of a weak potash lye; the rest of the process is the same as just described. A third observer, Sinclair, relates that the bark is boiled for half an hour with water: some alum and carbonate of potash are then added to the decoction, which is poured away from the sediment. The stuffs are dyed in the clear fluid; they must be dipped repeatedly, and the pieces must be spread frequently upon the turf, in order to obtain a deeper shade.

Notwithstanding the contradictions in the above reports, it appears to be certain that the bark serves for dyeing cotton, and that the intensity of the colour is essentially increased by the influence of light, for which reason frequent exposure on the turf is necessary. Mercer of Oakenshaw and Persoz expressed the opinion independently of each other, that the colouring matter is applied upon one side only of the tissue, as they concluded from the inspection of true China-dyed pieces. This opinion, however, has now proved to be positively erroneous, and it is to be assumed that the above reports are correct in the main.

b. *Preparation of Lo-kao.*—It is somewhat surprising to learn in how troublesome a way the Chinese prepare the dye-material, which made so much noise in our silk-dyeing establishments, and yet numerous eye-witnesses agree in their accounts of the manufacture

of Lo-kao. It is said to be effected as follows:—Pieces of cotton stuffs are repeatedly passed through the dye-vats as above described, and dried after each dyeing; so that, until they are quite ready, they are never washed. This operation is not performed until they are positively overloaded with colouring matter, when they are washed in cold water, which is then boiled with a layer of cotton yarn at the surface of the fluid. During the boiling of the fluid the colouring matter is deposited on the yarn, and the coloured fluid is changed until the yarn is very strongly covered with colouring matter, when it is thoroughly washed in a little cold water. The colouring matter settles in the water, and the paste is spread upon sheets of paper laid upon a stratum of ashes, and dried in the sun.

From these statements we learn that the Lo-chou dyeing must have acquired a great extension in China; for the production of 800—900 kilogrms. of Lo-kao presupposes that at least 1 million of pieces must have been dyed in the decoction of the bark, and more than 500 kilogrms. of this dye-stuff were imported into France alone in the year 1857.

c. *Lo-kao for dyeing Cotton Fabrics.*—Two eye-witnesses relate the remarkable fact that, notwithstanding the dearness of the material, cotton stuffs are dyed with it; and the pay of the dyers is not higher than for dyeing with Lo-chou bark. But the Lo-kao is used for lighter shades, and when employed is dissolved in solution of potashes, into which the stuffs are passed twice, wrung, washed, and dried. A weight of 38 grms., or about 1 ounce, is said to be sufficient for dyeing from 10 to 30 pieces of cotton stuff.

d. *Lo-kao for dyeing Silk and Silk Fabrics.*—Although Father Helot states that Lo-kao cannot be employed in silk-dyeing, it is ascertained that the first samples of this drug brought to Europe were purchased from Chinese silk manufacturers and silk dyers. Moreover, several reports are in existence in which we are assured that Lo-kao is also used in dyeing silk, and indeed the silk fabrics dyed therewith are more highly valued than those dyed with the bark; but it may still be true that this substance is best adapted to perfectly smooth grounds, such as fine cotton stuffs and grass cloth. However this may be, we are not acquainted with the solvent employed by the Chinese for this substance, but it is certain that in Europe, at least in Lyons, dyeing with Lo-kao is well understood. As early as the year 1853, and indeed nearly simultaneously, Michel and Guinon discovered a process by means of which the Lo-kao green may be applied to silk. The former has published his process; the latter, who sent samples of satin dyed with Lo-kao to the Exposition of 1855, still keeps his process a secret. In the year 1855–56 Guinon dyed 1500 kilogrms. of silk with the Chinese green; in the year 1856–57 they applied this dye to 3500 kilogrammes of silk.

The Chemical and Physical Properties of Lo-kao, by Persoz.—The Chinese green forms flat, somewhat curved discs of a thickness of 1—4 millims., and of various sizes, according as it has been more or less broken up by transport. Its colour is blue with a surface-

tinge of violet and green; when rubbed on paper it gives a green streak. It is brittle, but nevertheless is powdered with difficulty, as it adheres firmly to the pestle and mortar.

When incinerated it furnishes between 21·5 and 33 per cent. of residue. Persoz found—

61·9 per cent. of colouring matter,
28·8 „ of ash, and
9·3 „ of water.

Professor Bleekrode found the ashes to be composed of—

Clay	52·58
Lime	31·16
Phosphates of lime and iron	12·45
Alumina	2·58
Phosphates of potash and soda	1·23

The colouring matter could not by any means be separated by sublimation from the mineral constituents.

Volatile oils, alcohol and æther, acetone, and sulphuret of carbon have no action upon Lo-kao.

This colouring matter may be very finely divided in water, without positively dissolving therein; it is true that a green fluid passes through the filter, but the greater part of the colouring matter remains upon the filter. If we have a concentrated aqueous solution, or rather suspension, of the colouring matter in distilled water, the addition of a further quantity of water to this soon throws down the colouring matter.

A solution of the colouring matter may be effected by means of the acid salt of tin; this keeps for some time, but on the addition of water, a flocculent precipitate of a poppy-red colour separates.

Solutions of the alkaline carbonates, borates, and phosphates may also be employed as solvents for Lo-kao, but as soon as the fluids are diluted, the colouring matter is again thrown down, but in a purer state than before.

It is also worthy of remark that a solution or suspension of Lo-kao in water soon becomes essentially altered. Its colour becomes blood-red, and a somewhat hepatic odour manifests itself; this is a process, hitherto unexplained, similar to that which is observed with other solutions of colouring matters, such as alkanet.

Acetic acid is an agent which assists the solubility of Lo-kao, perhaps by the formation of acetate from the bases of the Lo-kao. Dilute muriatic, sulphuric, and tartaric acids may have a similar action, but their contact with the dye-stuff must not continue too long, and the solution must not be boiled.

If Lo-kao be boiled with dilute muriatic acid, or brought in contact with concentrated acid at ordinary temperatures, an iron-grey precipitate is thrown down, and a yellow solution is formed over it; the latter is tolerably stable under the action of acids, but is rendered orange by alkalies. The iron-grey precipitate contains earthy constituents which it is very difficult to get rid of. With ammonia it becomes blue or violet, with sulphuret of ammonium purple red,

with protochloride of tin salmon colour; in boiling solution of soap it is dissolved with a green colour, which is converted into red by sulphuret of ammonium, and into rose-colour by solution of tin-salt.

The acids with a reducing action, such as the phosphorous, sulphurous, arsenious, formic acids, &c., have a very rapid action, partly even at ordinary temperatures, and partly when heated, upon Lo-kao, producing a blood-red precipitate in its solutions. Sulphuretted hydrogen colours the solution blood-red, but this colour disappears again when no excess of sulphuretted hydrogen is left in the solution.

Oxidizing acids, such as nitric, chloric, hypochlorous, chromic acids, &c., all have an alterative action upon the colouring matter; it passes through various changes of colour, and becomes at last rose-red. This red, however, is not the same as that produced by reducing acids, for whilst a green may be reproduced from the latter, this is impossible with oxidizing acids. The caustic alkalies, even lime-water, have a destructive action upon the green colouring matter; it is converted (by the latter only when boiled) into a brown solution, with which cotton treated with a tin or alum mordant may readily be dyed. Solutions of the alkaline carbonates act in the same way at high temperatures, and this is also the case with the alkaline sulphurets. Sulphuret of ammonium is one of its most energetic reducing agents and solvents, so that it may serve both as a reagent for Lo-kao and also in dyeing. Zinc and magnesia salts rapidly change the green solution of Lo-kao into blue. If cotton be dyed in a solution of Lo-kao mixed with chloride of zinc, it becomes blue, nearly the same as vat blue. Solution of alum assists the solubility of Lo-kao; the solution becomes blue.

Lo-kao exhibits a peculiar reaction towards perchloride and protochloride of tin and other metallic salts, which may be decomposed by sulphuretted hydrogen. If the above-mentioned red precipitate be produced by diluting an acid solution of Lo-kao and tin-salt, suspended in water after being well washed, and then treated with sulphuretted hydrogen, it would be expected that sulphuret of tin would be formed, and that the colouring matter would dissolve with the change of colour produced by sulphuretted hydrogen, but this is by no means the case; the fluid remains colourless, but the precipitate becomes orange-coloured, without any formation of sulphuret of tin.

Applications.—Persoz decidedly expresses the opinion that dyeing with Lo-kao will be best effected upon mordanted stuffs; the crude Lo-kao indeed fixes by virtue of its own earthy constituents, even upon unmordanted spots, but the purified material, to which, however, the dyer should always give the preference, only dyes mordanted fibres.

Purification of Lo-kao.—This may be effected in two ways:—A concentrated solution of it is prepared either in solution of carbonate of potash or in acetic acid. By diluting either of these solutions, the colouring matter is soon thrown down (not perfectly free from earthy matter) in light flakes which may be employed in dyeing.

Blue Colour-lakes from Chinese Green.—An *aluminous lake* may be prepared in three ways. A solution of Lo-kao with solution of alum is prepared, and the green lake is thrown down therefrom by solution of carbonate of soda; or a solution of Lo-kao in an alkaline carbonate is prepared and precipitated by solution of alum; or a solution of basic alum is mixed with an aqueous solution (suspension) of Lo-kao, and the whole is boiled. The precipitate is collected and kept in a moist state; it may be employed in dyeing and printing.

Tin-lake.—When a solution of tin-salt and muriate of ammonia is poured into a solution of Lo-kao in water or acetic acid, and a little acetate of soda is then added, a fine blue precipitate is formed.

Lime-lake.—If a solution of Lo-kao which has been standing for some time and has been treated with a reducing acid, and in which the above-mentioned change of colour has taken place, be mixed with a solution of acetate of lime, a precipitate is obtained of a deep blue colour, with a tendency to violet.

The above-mentioned three lakes may find their application in dyeing or stuff-printing.

Dyeing with Lo-kao: Silk-dyeing.—The process of Michel, a dyer at Lyons, consists in drawing the scoured silk several times through a rather hot solution of Lo-kao, mixed with alum. For this purpose we may employ the crude or purified Lo-kao, or its aluminous lake.

Another process which is praised by Persoz, although he regards Michel's as excellent, is as follows:—The silk to be dyed is passed through a bath of Lo-kao and tin-salt, with the addition of a little muriatic acid at ordinary temperatures. It merely acquires a salmon colour, but when taken, it is passed through an alkaline bath mixed with ammonia or solution of carbonate of potash, or through a bath containing a little acetate of lime and an excess of lime-water. By this means the pale red passes through purple-red to blue. After washing in cold water and wringing, it is again passed through a decoction of Persian berries, in order to produce an agreeable green. It is a remarkable circumstance in this process, that when the blue has a tinge of violet, the green does not appear more brilliant by artificial light. Silk may also be mordanted with alum and passed through a solution of Lo-kao in sulphuret of ammonium, hanging the silk up in the air after each bath, until the red has become green.

Lastly, the Lo-kao may be dissolved in stannate of soda, and the silk dyed in this solution; when taken out of the bath, it has become of a tolerably deep bluish green.

Cotton-dyeing.—Lo-kao is suspended in water, and to this an alkaline salt, such as carbonate of soda, or some alum or magnesia, or a solution of a salt of zinc is added. It is heated to 104°—140° F., and on the addition of a salt of zinc, a more bluish, on the addition of alkaline carbonates or borates, a more greenish shade is obtained. The following, however, is perhaps the best process: 50—60 grms. of white soap are dissolved in 10 litres of water, and

a suitable quantity of purified or moistened Lo-kao is diffused through it. The bath is then heated, when simple immersion is sufficient to dye the cotton directly.

For printing, all that is necessary is to diffuse the Lo-kao or its aluminous lake in mucilage of gum, and to add a little acetate of alumina or common alum. The latter, however, may be left out.

Wool.—Dyeing with Lo-kao upon wool is more difficult than upon silk and cotton; it may, however, be readily effected by the following process:—The above-mentioned tin-lake is diffused in water, the bath is heated with the gradual addition of a few drops of oxalic acid, and the wool immersed in this bath is perfectly dyed.

The experiments of Michel upon the possibility that the European species of *Rhamnus* may furnish a dye analogous to Lo-kao, have hitherto led to no result which can be regarded as conclusive, but, even in the opinion of Persoz, they leave no doubt with regard to the Chinese process. There is no more reason to suppose that the Chinese green cottons are coloured by an application to one side. Michel expresses a hope that the best results may be looked for from the bark of three indigenous species of *Rhamnus*; namely, *R. catharticus*, which furnishes the well-known sap-green, *R. infectorius*, from which the Avignon berries are obtained, and *R. saxatilis*, the source of the true Persian berries, and therefore three species of spiny, shrubby *Rhamni*. He himself dyed pieces of calico by a process exactly similar to that described by Helot as employed by the Chinese, namely, frequent passage through the bath, and exposure during the night and early morning; these all had a greyish-brown tinge but exhibited a right and wrong side. The species employed by him were *R. alaternus*, *R. frangula*, and *R. catharticus*. The greyish-brown tinge could be removed from all his samples by a subsequent treatment with hot solution of alum. This extracts the yellow and tawny tints, but also a portion of the green, but the latter was again thrown down upon the fibres when the stuff was left in the bath until it got cold.—*Polytechnisches Centralblatt*, 1859, p. 261, and *Chemisches Centralblatt*, 1859, p. 193.

PROCEEDINGS OF SOCIETIES.

Royal Society.

March 10, 1859. (Sir Benjamin C. Brodie, Bart., Pres., in the Chair.)

"New Volatile Organic Acids, from the Berry of the Mountain Ash." By A. W. Hofmann, LL.D., F.R.S.

Whoever has been engaged in the preparation of malic acid from the juice of the unripe berries of the Mountain Ash (*Sorbus Aucuparia*), cannot have failed to perceive the peculiar powerful odour evolved during the evaporation of the liquid partially saturated with lime. The body to which this odour belongs was hitherto unknown, and only lately, my friend and former pupil, Dr. George

Merck of Darmstadt, when preparing malic acid on a large scale, conceived the happy idea of evaporating the liquid in a distilling apparatus. He thus obtained an acid distillate, from which he succeeded in separating an oily body possessed of acid properties. To the kindness of Dr. Merck I am indebted for an appreciable quantity of this remarkable body, which has enabled me to examine its properties and establish its composition.

The preparation of the oil from the aqueous acid obtained by distilling the mother-liquor of the bimalate of calcium, presents no difficulty. The liquid is saturated with soda, evaporated and mixed with dilute sulphuric acid, when the oil rises as a brown layer to the surface of the liquid. It is separated by ether, and after the volatilization of the latter, submitted to distillation. The first portions of the distillate contain appreciable quantities of water; the thermometer, however, rapidly rises above 200° C. What now distils is a perfectly pure compound, which, on redistillation, exhibits a constant boiling-point at 220° C. Freshly distilled, the oil is colourless, but it soon acquires a yellowish tint. It has a peculiar aromatic odour, not disagreeable when dilute, but rather offensive when concentrated. The specific gravity is 1·0681. It is somewhat soluble in water, very soluble in alcohol and ether; these solutions are distinctly acid. The oil dissolves in potassa and ammonia, also in the carbonated alkalies, without, however, expelling their carbonic acid. Mineral acids separate it again from these compounds.

The analysis of the oil shows that it contains carbon, hydrogen, and oxygen in the ratio of

$$C_3 H_2 O;$$

but the determination of the silver in a white amorphous silver compound, obtained by adding nitrate of silver to the ammoniacal solution of the oil, shows that this expression must be quadrupled, and that the acid and silver salt are represented by the following formulæ:—

$$\text{Acid} \quad . \quad . \quad C_{12} H_8 O_4$$
$$\text{Silver-salt} \quad C_{12} [H_7 Ag] O_4.$$

The acid oil of the mountain-ash berry exhibits a very remarkable deportment with the alkalies and acids. When gently heated (a temperature of 100° is sufficient) with solid hydrate of potassa, or when boiled with concentrated hydrochloric or moderately dilute sulphuric acid, the oil is readily converted into a splendid crystalline acid, greatly resembling benzoic acid in its general characters, which has the same composition as the oil itself. I have established this remarkable isomerism both by careful observation of the conditions of transformation, and by the analysis of the crystalline acid as well as of some of its salts and derivatives. I propose to designate this new compound by the term sorbic acid, thus reviving an old name which had at one time been used for malic acid. The isomeric oil obtained by distilling the juice of the mountain-ash berry, the acid properties of which are much less pronounced, may then be called Parasorbic acid.

Sorbic acid.—This substance is readily soluble in alcohol and ether, less so in water. Heated with a quantity of water insufficient for solution, it fuses; the aqueous solution, saturated by ebullition, solidifies on cooling into a network of interlaced needles. The acid crystallizes best from a mixture of alcohol and water, in which the latter predominates; from this solvent it is often deposited in magnificent needles several inches in length. Sorbic acid fuses at 134°·5. It boils at a much higher temperature, and may be volatilized without decomposition.

The alkaline sorbates are all soluble in water, the potassium, sodium, and ammonium compounds are extremely soluble, and crystallize with difficulty; the barium and calcium salts are less soluble, and may be obtained in splendid scaly crystals of the lustre of silver. Their crystallization is facilitated by the addition of a small quantity of alcohol. Both salts are anhydrous, their analysis agreeing with the formulæ

Sorbate of barium . . . . . $C_{12}[H_7 Ba]O_4$
Sorbate of calcium . . . . . $C_{12}[H_7 Ca]O_4$.

The silver-salt is a white amorphous precipitate, extremely insoluble in water, readily obtained by the decomposition of the ammonium compound by nitrate of silver. Both combustion and silver-determination proved this salt to be

Sorbate of silver . . . . . $C_{12}[H_7 Ag]O_4$.

The ether of sorbic acid is readily procured by treatment of the alcoholic solution of sorbic acid with hydrochloric acid, or by the action of chloride of sorbyle upon alcohol. It is a colourless liquid of an agreeable aromatic odour resembling that of benzoic ether, boiling at 191° C., and containing:—

Sorbate of ethyle $C_{16}H_{12}O_4 = C_{12}[H_7(C_4H_5)]O_4$.

The experiments which I have quoted are sufficient to fix the composition of sorbic acid. I have nevertheless produced some additional derivatives of the acid.

Chloride of sorbyle is obtained by the usual processes; by the action of pentachloride of phosphorus upon the acid, or of the trichloride of phosphorus upon the potassium compound. The limited amount of acid at my disposal did not permit me to procure this substance in a state of purity, and to establish analytically the formula

$$C_{12}H_7O_2Cl$$

assigned to it by theory; but this formula is indirectly proved by the deportment of the crude product, still containing chloride of phosphorus—with water, when sorbic acid is at once reproduced;—with alcohol, when sorbic ether is obtained;—with ammonia and phenylamine, when respectively, sorbamide and phenyl-sorbamide are generated. The chloride is not volatile without considerable decomposition.

Sorbamide.—This substance is formed by the action of dry carbonate of ammonium upon the crude chloride of sorbyle. White,

readily fusible needles, soluble in water and alcohol. Composition of

$$\text{Sorbamide } H_{12}H_9NO_2 = \left.\begin{matrix} C_{12}H_7O_2 \\ H \\ H \end{matrix}\right\} N.$$

Phenyl-sorbamide is obtained by replacing the ammonia in the previous process by phenylamine. After treatment with water an oily liquid remains, which gradually solidifies into a crystalline mass. I have not analysed it, its composition being sufficiently characterized by theory.

When distilled with an excess of hydrate of baryta, sorbic acid exhibits the deportment of the acids with four equivalents of oxygen; carbonate of barium is produced, whilst an aromatic hydrocarbon distils over. The limited amount of material has precluded for the present the possibility of a more minute examination of this body.

Sorbic acid is obviously the first term of a new series of well-characterized organic acids, closely allied to the ordinary fatty and aromatic acids, occupying, in fact, a sort of intermediate position between the two. On comparing sorbic acid with the terms of the fatty and aromatic acid-series containing equal quantities of carbon, the hydrogen of sorbic acid stands in the middle,

$\underbrace{C_{12}H_{12}O_4}$	$\underbrace{C_{12}H_8O_4}$	$\underbrace{C_{12}H_4O_4}$
Caproic acid.	Sorbic acid.	Lower homologue of benzoic acid.

The same remark applies to the carbon of sorbic acid when contrasted with the fatty and aromatic acids containing an equal quantity of hydrogen,

$\underbrace{C_8H_8O_4}$	$\underbrace{C_{12}H_8O_4}$	$\underbrace{C_{16}H_8O_4}$
Butyric acid.	Sorbic acid.	Toluic acid.

"Further Remarks on the Organo-metallic Radicals Mercuric, Stannic, and Plumbic Ethyle."—No. III. By George Bowdler Buckton, Esq., F.R.S., F.L.S., F.C.S.

On resuming my inquiries into the nature of these organo-metals, I have met with some interesting reactions, which I here wish briefly to notice.

The preparation of mercuric, stannic, and plumbic ethyles, through the action of zincethyle on various organic and inorganic salts, has been already detailed in my sketch published in the 'Proceedings of the Royal Society*;' but at that time, I was not able to fix, with certainty, the constitution of the compounds which were produced by acids on the different radicals. An appeal to analysis now enables me to state the following

Mercuric ethyle.

The reactions of this liquid are well-marked. Towards sulphuric and hydrochloric acids it follows the deportment of its homologue

* Chem. Gaz. vol. xvi. p. 415.

mercuric methyle. When assisted by gentle heat, one equivalent of ethyle is disengaged, which unites with the hydrogen of the acid, and forms hydride of ethyle, whilst the acid takes its place, and gives rise to the corresponding salt of mercurous ethyle.

The radical bursts into flame when poured into chlorine gas, and is almost entirely destroyed; but when it is slowly mixed under water with iodine or bromine, the disengagement of ethyle gas is scarcely perceived, and iodide or bromide of ethyle may be recovered by distillation.

$$\underbrace{4\,(Hg\,C_4\,H_5)}_{\text{Mercuric ethyle.}} + 2\,H\,SO_4 = \underbrace{2\,(Hg_2\,C_4\,H_5)\,S_2O_5}_{\text{Sulphate of mercurous ethyle.}} + \underbrace{2\,(C_4\,H_5\,H)}_{\text{Hydride of ethyle.}}$$

$$\underbrace{2\,(Hg\,C_4\,H_5)}_{\text{Mercuric ethyle.}} + 2\,Br = \underbrace{Hg_2\,C_4\,H_5\,Br}_{\text{Bromide of mercurous ethyle.}} + \underbrace{C_4\,H_5\,Br}_{\text{Bromide of ethyle.}}.$$

From considerations connected with the vapour density of mercuric ethyle and mercuric methyle, as given by experiment, there seem to be reasons for believing that the formulæ of all the organo-metals of this group should, in correctness, be doubled. I have not, however, yet been able to satisfy these views by direct experiment. Zincethyle acts readily on salts of mercurous methyle; and in all probability gives a body compounded of ethyle and methyle with a double equivalent of mercury $\left.\begin{matrix} Hg\,C_4\,H_5 \\ Hg\,C_2\,H_3 \end{matrix}\right\}$. The substance, however, if produced, is obviously broken by distillation into the two radicals mercuric ethyle and mercuric methyle. Experiment may perhaps prove more successful if salts of stannic methyle be similarly treated.

The electro-negative character of the group $C_{n2}\,H_{n2+1}$ in the class of organo-metals to which zincethyle belongs, may now perhaps be considered as established. Some interest, nevertheless, attaches to the question whether sodium is capable of displacing ethyle from mercuric ethyle. An answer to this question would give us some means of judging the position of ethyle, as regards its electro-negative function towards the true metals.

At ordinary temperatures, sodium has only a slow action on mercuric ethyle, but after the lapse of a few hours a voluminous grey sponge is formed, whilst the liquid entirely disappears. This sponge-like body has the property of spontaneous combustibility in a marked degree, and is liable to explosion from apparently very slight causes. By the application of a gentle heat, a strong rush of gaseous matter is evolved which eudiometric experiments proved to be a mixture of ethylene and hydride of ethyle, obviously proceeding from the disintegration of a double molecule of ethyle.

From this experiment we should conclude that ethyle, methyle, &c. in these radicals are still negative to mercury, and therefore, that mercury, copper, &c. would not, as Mr. Wanklyn supposes, displace ethyle in sodiumethyle*. More probably, perhaps, sodiumethyle is

* Chem. Gaz. vol. xvi. p. 459.

first formed in the reaction,

$$Hg\,C_4\,H_5 + Na = Na\,C_4\,H_5 + Hg,$$

and then decomposed by heat,

$$2\,(Na\,C_4\,H_5) + 2\,Hg = 2\,Na\,Hg + C_4\,H_4 + C_4\,H_5\,H.$$

The mercury is supposed here to be inert, and in no way to determine the decomposition.

Stannic diethyle.

Much of the uncertainty which has attached to some of the formulæ of the salts of stanethyle, has originated, without doubt, from the mode adopted by Löwig in their elimination. Strecker has lately shown that many of these compounds may, with probability, be referred to the types of the inorganic oxyiodides and oxychlorides of tin.

The following experiments were undertaken with the impression that the pure salts of stanethyle might be more advantageously procured by acting directly on the radical itself.

Stannic diethyle, $Sn\,(C_4\,H_5)_2$, like mercuric ethyle, loses one of its equivalents of ethyle when digested with concentrated acids. The action, however, is very slow with hydrochloric acid, an oily body being first formed, possessed of an exceedingly pungent odour; but finally a chloride is obtained having the formula

$$Sn\,C_4\,H_5\,Cl.$$

This salt produces fine, hard crystals, which are soluble in water, and, when pure, almost inodorous. A more ready method of obtaining this chloride consists in adding the radical, drop by drop, to a layer of bromine covered with water, until the bromine is decolorized; the aqueous solution is then decomposed by potash, which precipitates oxide of stanethyle in the form of a white powder, from which the pure salts of stanethyle may be readily procured.

The solubility of these salts in aqueous potash has been rather variously stated by Löwig and Frankland, and also their characters as odorous and inodorous. The truth is, that unless the salts of stanethyle are formed from the oxide, they are almost always contaminated with the above-mentioned oily chloride, the oxide of which is soluble in potash. As oxide of stanethyle is not affected by alkaline solutions, these two bodies may be separated without difficulty.

The soluble oxide may be recovered from the alkaline solutions by distillation. It passes over, together with aqueous vapour, in the form of an exceedingly caustic and pungent oil, which blues litmus, and has all the characters of a powerful base. Water dissolves it in moderate quantities, but precipitates it again on the addition of common salt. When deprived of water, the oily base solidifies into a crystalline mass.

This oxide forms definite salts with acids, all more or less pun-

gent. With hydrochloric and hydriodic acids, uncrystallizable bodies, insoluble in water, are produced, but with sulphuric acid it forms fine, colourless crystals, which by analysis gave the formula

$$Sn_2 C_{12} H_{15} SO_4 \text{ or } Sn_2 (C_4 H_5)_3 SO_4.$$

For this compound I propose the name of sulphate of distannic triethyle. It has, in a remarkable degree, the unusual property of being more soluble in cold than in hot water. A cold saturated solution becomes semi-solid by raising the temperature somewhat below ebullition.

A consideration of the elements of the above formula furnished an idea of these bodies being either double salts, compounded of one equivalent of stannic diethyle with one equivalent of any salt, $Sn C_4 H_5 X$, or else a combination of three equivalents of stannic diethyle, with one equivalent of an inorganic salt $Sn X_2$, resulting in two molecules of the sesqui-ethylated salt. Thus

$$3 Sn (C_4 H_5)_2 + Sn Cl_2 = 2 Sn_2 (C_4 H_5)_3 Cl.$$

Experiment proves that the former bodies mix, but do not combine chemically, at any moderate heat. The latter bodies, on the other hand, exhibit strong chemical action, and disengage great heat during combination.

Bichloride of tin forms an oily body with stannic diethyle, chiefly composed of chloride of distannic triethyle, which by treatment with potash may be made to furnish the corresponding salts without difficulty.

Iodide of distannic triethyle may often be found amongst the products of the action of tin on iodide of ethyle. It is very probably identical with the oil noticed by Riche and Cahours, and described by them as possessing the pungent odour of oil of mustard.

These salts also must be considered to be identical with those described by Löwig under the somewhat inappropriate name of "methylo-stanethyles." The present name is suggested as more in accordance with their true constitution. They finally pass, by the action of zincethyle, into the radical stannic diethyle.

The presence of iodide of distannic triethyle amongst the stannic bodies in Löwig's experiments can be satisfactorily accounted for, by presuming the incomplete reduction of the iodides by the alloy of tin and sodium, employed in the reactions.

The behaviour of zincethyle towards the chlorides of tin may be expressed, step by step, by the following equations, the tin-salt being supposed to be added to the zincethyle:—

$$\text{I.} \quad 2 Zn C_4 H_5 + Sn Cl_2 = Sn (C_4 H_5)_2 + 2 Zn Cl$$

$$\text{II.} \quad 3 Zn C_4 H_5 + 2 Sn Cl_2 = Sn_2 (C_4 H_5)_3 Cl + 3 Zn Cl$$

$$\text{III.} \quad Zn C_4 H_5 + Sn Cl_2 = Sn \; C_4 H_5 \; Cl + Zn Cl; \text{ also}$$

$$\text{IV.} \quad 2 Zn C_4 H_5 + Sn Cl = \underbrace{Sn C_4 H_5 + Zn C_4 H_5}_{\text{Double compound ?}} + Zn Cl.$$

I have failed in satisfactorily separating the radical stannic ethyle from the excess of zincethyle, as represented in the last reaction. By

the addition of water great heat is generated, and tin is thrown down in its metallic state.

By distillation also, the radical stannic ethyle is similarly broken up,

$$2\,Sn\,C_4\,H_5 = Sn\,(C_4\,H_5)_2 + Sn.$$

Plumbic diethyle.

In the abstract above alluded to, I have stated the difficulties which at that time prevented my obtaining the lead radical in a state of purity. This difficulty arises from its tendency to decompose suddenly at a point below that of ebullition. This disadvantage is entirely obviated by conducting the distillation *in vacuo*, or at least under reduced atmospheric pressure. The organo-metal was found to distil unchanged under a pressure of 7·5 inches of mercury at a temperature of 152° C., the barometer at 30·5 inches. This is a remarkable lowering of the boiling-point, which at ordinary atmospheric pressures appears to be a few degrees above 200° C.

Analysis gave numbers leading to the formula

$$Pb\,C_8\,H_{10} \text{ or } Pb\,(C_4\,H_5)_2.$$

Plumbic diethyle is a limpid and colourless fluid, possessing a specific gravity of 1·62. It burns with an orange flame, tinged at the edges with pale green, and disengages whilst burning much oxide of lead.

The only salts hitherto prepared from this radical seemed formed on the type of the sesquioxides. By passing excess of hydrochloric-acid gas over the organo-metal, hydride of ethyle is liberated, and chloride of diplumbic triethyle is obtained.

$$2\,Pb\,(C_4\,H_5)_2 + H\,Cl = Pb_2\,(C_4\,H_5)_3\,Cl + C_4\,H_5\,H.$$

The chloride is a fine crystalline body, occurring in long needles, which fuse at a gentle heat, and then take fire, with the characteristic lead flame.

Oxide of diplumbic triethyle may be obtained by heating any of the corresponding salts with strong potash, or by acting on a solution of the chloride with oxide of silver. It is a crystalline body, which fuses into an oil-like liquid, at a gentle heat.

Sulphuric acid forms an abundant crop of asbestos-like needles when mixed with a warm solution of the chloride of diplumbic triethyle. It may also be obtained by neutralizing a solution of the oxide, and also by the action of sulphate of silver on the chloride.

Analysis furnished numbers which pointed to the formula

$$Pb_2\,C_{12}\,H_{15}\,SO_4 \text{ or } Pb_2\,(C_4\,H_5)_3\,SO_4.$$

All the salts of this sesqui-ethylated base are volatile, and their vapours attack the eyes and mucous membrane of the throat. In this respect they imitate their homologues in the stannic series.

In concluding this short abstract, I will only express my belief that a wide field of research is still open for inquiry, and that some promising experiments are at present in hand, from the right understanding of which we may hope to throw additional light on these interesting substances.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Cresylic Alcohol. By Lucien Duclos.

According to Fairlie coal-tar contains, besides phenylic alcohol, $C^{12}H^6O^2$, another alcohol which he calls cresylic alcohol, and which, according to him, has the formula $C^{14}H^8O^2$, and would therefore be isomeric with benzylic alcohol.

The author has investigated this body in Will's laboratory. He prepared cresylic alcohol by the process described by Fairlie, from coal-tar creosote, and from the wood-tar of the gas-works at Giessen.

The wood-tar was distilled by itself, and the portion passing between 302° and 428° F. and containing the creosote, was treated with concentrated solution of soda in order to remove the hydrocarbons; this treatment was repeated with the product separated by dilute sulphuric acid from the alkaline solution until this dissolved completely and formed a clear solution in solution of soda. After washing with water and drying over chloride of calcium, it was submitted to fractional distillation.

The portion boiling at 369° F. and consisting of phenylic alcohol, was collected separately from that boiling at 397° F., which contained cresylic alcohol.

The cresylic alcohol thus prepared, $C^{14}H^8O^2$, had all the properties ascribed to it by Fairlie. The author, however, found, that, in opposition to the statement in Gerhardt's 'Traité de Chimie Organique,' iv. p. 1029, cresylic alcohol is not perceptibly less soluble than phenylic alcohol in ammonia.

Hydrate of cresyle is miscible in all proportions with alcohol and æther. Fir-wood, soaked in its aqueous solution, and then moistened with muriatic acid, acquires a blue colour when exposed to the sun's light. Nitric acid, whether cold or hot, produces a violent reaction with it, and furnishes a brown uncrystallizable substance. Potassium and sodium, when gently heated, evolve hydrogen gas, and the

brownish compound, on cooling, solidifies into a deliquescent crystalline mass, consisting of small needles, which can only be obtained pure with difficulty even by recrystallization from æther and evaporation *in vacuo*. In concentrated sulphuric acid, hydrate of cresyle dissolves with a reddish colour, and with formation of sulphocresylic acid. At about 140° F. the conversion is completed in about 24 hours; the mass then dissolves in water without any separation of oil drops.

The author's analyses agree with the formula given above.

If cresylic alcohol be mixed with concentrated sulphuric acid, and the dilute fluid be subsequently saturated with carbonate of baryta, we obtain sulphocresylate of baryta, of which the formula is

$$C^{12}\,H^{7}\,BaS^{2}O^{8}.$$

By heating the aqueous solution of cresylic alcohol to 140°—156° F. and then adding dilute nitric acid, we obtain

Mononitrocresylic Acid, $C^{14}\,H^{7}\,(NO^{4})\,O^{2}$, in the form of a yellowish-brown oil of a syrupous consistence. It is inodorous, but has a bitter taste.

If sulphocresylic acid, diluted with five or six times its volume of water, be heated with the addition of a little nitric acid diluted with an equal volume of water, we get

Dinitrocresylic Acid, $C^{14}\,H^{6}\,(NO^{4})^{2}\,O^{2}$, which is exactly similar to the preceding in its properties. When rapidly heated in a tube it explodes, but when carefully heated a portion evaporates apparently undecomposed. The ammoniacal salt of this acid, which is very soluble, is difficult to crystallize.

Trinitrocresylic Acid, $C^{14}\,H^{5}\,(NO^{4})^{3}\,O^{2}$, is obtained with the greatest ease and certainty by heating a dilute solution of sulphocresylic acid with a little nitric acid, separating the resinous body formed by filtration, and treating the filtrate again with nitric acid. The binitro-compound thus separated, is converted by the action of the nitric acid during evaporation into trinitrocresylic acid, which is contained, with oxalic acid, in the crystalline residue. By washing with water, the oxalic acid is removed; and the acid is obtained crystallized by solution in alcohol, and the evaporation of the solution *in vacuo*.

The formula is $C^{14}\,H^{5}\,(NO^{4})^{3}\,O^{2}$, as found by Fairlie. Trinitrocresylic acid crystallizes from alcohol, in which it is very soluble, in citron-yellow needles. At 68° F. it requires 449 parts, and at a boiling heat 123 parts of water for its solution; picric acid, according to Marchand, dissolves in 80 parts of water at 68° F., and in 21 parts at 170° F. Trinitrocresylic acid is also soluble in æther and benzole. The aqueous solution, which is of a fine yellow colour, reddens litmus; silk and wool are dyed yellow by it. When heated to a little above 212° F., the acid fuses into a reddish-yellow oil, which solidifies in a crystalline form on cooling; when more strongly heated, it explodes in the same way as picric acid. On the addition of a mineral acid to a saturated aqueous solution, a portion of the trinitrocresylic acid separates; but the acid is more soluble in an

excess of nitric acid when heated, than in water. When heated with solution of chloride of lime, or with chlorate of potash and muriatic acid, it evolves the odour of chloropicrine.

Trinitrocresylate of Ammonia, $C^{14} H^4 (NO^4)^3 (NH^4) O^2$, is obtained by saturating the acid with ammonia, and evaporating the solution; it forms yellow needles, readily soluble in water, less soluble in alcohol, which explode when heated.

Trinitrocresylate of Potash, $C^{14} H^4 (NO^4)^3 KO^2$, is obtained by saturating the acid with carbonate of potash, in small needles which are very soluble in water, and detonate strongly when heated.

If a boiling dilute solution of acetate of lead be mixed with trinitrocresylate of ammonia, and the precipitate produced be separated by filtration, yellow microscopic needles separate from the filtrate; these dissolve readily in water, and explode when heated. The analysis of this salt gave 45·34 per cent. of lead (0·1974 gave 0·1318 of sulphate of lead). The formula $C^{14} H^4 (NO^4)^3 PbO^2 + PbO$ requires 45·59 per cent.—Liebig's *Annalen*, cix. p. 135.

Formation of Protoxide of Copper. *By* O. L. Erdmann.

If an ammoniacal solution of a persalt of copper be left standing in contact with metallic copper with the air not completely excluded, a reduction of the dissolved oxide takes place, but the fluid is not totally deprived of colour, for the protoxide constantly takes up oxygen from the air. After standing for weeks or months, a yellowish-brown precipitate of hydrated protoxide of copper is formed in the vessel. This latter body appears to be very sparingly soluble even in a great excess of ammonia unless an acid be also present; an addition of muriate of ammonia or a little acid dissolves it at once. This behaviour of an ammoniacal solution of oxide of copper furnishes a reason why Levol's copper-test rarely gives good results.—*Journal für Prakt. Chemie*, lxxv. p. 211.

On Umbelliferone. *By* Carl Sommer.

The author has investigated the Sumbul root in Zwenger's laboratory. The chopped root was extracted with æther, and the balsam of an agreeable odour, remaining after the evaporation of the last residue of the æther, was distilled with water, by which means, however, only a few drops of a pale yellow, essential oil were obtained. The latter is lighter than water, and but sparingly soluble therein; in alcohol and æther, on the contrary, it dissolves readily. The solution has a neutral reaction, but becomes rapidly resinified in the air, at the same time becoming acid, more thickly fluid, and darker. In the concentrated state its odour is very intense, presenting a closer resemblance to that of Angelica root than to that of musk; in more dilute solutions, on the contrary, the latter is more decidedly evident. When heated with nitric acid it dissolves with a violet colour, which afterwards becomes yellow; with concentrated sul-

phuric acid it acquires a brownish-yellow colour, and dissolves; when heated, carbonization takes places.

The residue in the retort, after this oil, of which only a small quantity is obtained, has been distilled off with water, is put into a porcelain capsule, and boiled until the water is evaporated. There remains a resin, which on cooling acquires a cracked aspect. The author submitted this resin to dry distillation. First of all one-third of a pale, subsequently greenish, thin oil with a distinct odour of creosote passes over; this is followed by thick, white vapours which readily condense into a blue oil, in which acicular crystals sometimes occur; these cover the neck of the retort with a radiating coat, and are also frequently held in solution by the oil. The blue oil was a mixture of various bodies, which could not be isolated. The crystallizable body is pressed between bibulous paper to free it from adherent oil, and then purified by crystallization from water. It is the author's

Umbelliferone, $C^{12}H^4O^4$, a neutral body. In reflected light its solution exhibits a blue surface colour, like that of æsculine. By the addition of aqueous alkaline fluids, the intensity of the blue colour is heightened, whilst acids in general cause its disappearance. The crystals dissolve with extraordinary facility in æther, alcohol, and chloroform.

Umbelliferone is tasteless and scarcely possesses any odour at ordinary temperatures, but when very gently heated, it evolves an odour which decidedly resembles that of cumarine, and the same odour is produced when the aqueous solution is boiled. When umbelliferone is more strongly heated, its odour presents much similarity with that of the wood of the wild cherry, and if it be heated to fusion, its vapour acquires an odour of cinnamon oil.

It fuses at rather a high temperature, namely at 464° F., forming a slightly yellowish oil, which solidifies completely on cooling in a crystalline form, and it may be sublimed without leaving any residue. The sublimation, however, commences before fusion, and it is therefore necessary, in order to avoid loss in analysis, to dry it in a closed space. Nitric acid converts umbelliferone into oxalic acid. Concentrated sulphuric acid dissolves it in the cold, with a bluish fluorescent colour, which appears more intense than that of the aqueous solution, probably because the quantity dissolved is much greater; when diluted with water, this colour disappears almost entirely, but again makes its appearance on the addition of a sufficient quantity of ammonia. When boiled with concentrated sulphuric acid, umbelliferone dissolves, forming a fluid with a dingy green surface-tint; when neutralized with baryta-water, the solution contains the umbelliferone undecomposed. Other acids, such as muriatic and acetic acids, also dissolve the crystals without decomposition, and on cooling they separate again unchanged. The dry crystals of umbelliferone are scarcely acted upon by chlorine; its aqueous solution is, however, rapidly decomposed by chlorine, with separation of a small quantity of a chocolate-coloured powder.

The author has selected the name of umbelliferone for this body,

because he has obtained the same substance, accompanied by blue oil, amongst the products of the dry distillation of the residue of the alcoholic extracts of other secretions procured from umbelliferous plants, such as galbanum, assafœtida, and gum panax; the so-called gum ammoniacum furnished no umbelliferone. He also obtained it by submitting the resins extracted by alcohol from the roots of *Ligusticum Levisticum*, Linn., *Angelica Archangelica*, Linn., *Meum athamanticum*, Jcq., and *Imperatoria ostruthium*, Linn., to dry distillation. The analyses of umbelliferone afforded—

	From Sumbul root, I.	Galbanum, I.	Asafœtida, I.	Asafœtida, II.	Sagapenum. I.
Carbon	66·67	66·54	66·46	66·75	66·58
Hydrogen	3·91	3·85	3·83	3·82	3·78
Oxygen	29·42	29·61	29·71	29·43	29·64

Archiv der Pharmacie, cxlviii. p. 1.

On the Electrolysis of Sulphuric Acid. *By* Dr. A. Geuther.

In order to answer the question whether an electrolyte of such a composition that it contains two elements in a different proportion than 1 : 1, is directly decomposed by the galvanic current, the author formerly made experiments with chromic acid, perchloride of iron, and bichromate of potash. He now describes a similar experiment made with the same object, in which anhydrous sulphuric acid was electrolysed.

Pure anhydrous sulphuric acid is not decomposed by the current of fourteen Bunsen's elements. On the other hand, the decomposition was effected when it was mixed with hydrated sulphuric acid, SO^3, HO. When a mixture of 4 parts of anhydrous sulphuric acid with 1 part of hydrate was employed, oxygen gas was evolved rather briskly at the positive pole, whilst no gas-bubbles were perceptible at the negative pole. The fluid, which possessed a brownish-yellow tinge, became perfectly colourless in that limb of the tube which contained the positive pole, whilst the slight coloration withdrew entirely into the other limb. When the action had been continued for a long time, blue streaks were perceptible ascending in the thick fluid from the negative pole; but these, although they increased by the duration of the action, always remained comparatively small.

When 3 parts of anhydrous and 1 part of hydrated acid were taken, the fluid obtained was a better conductor; more oxygen gas was evolved at the positive pole, and a slight evolution of gas was observed at the negative pole. Enlarged blue streaks soon showed themselves near the latter, so that the whole of the fluid in that limb of the tube appeared of a beautiful blue colour; at the same time an odour of sulphurous acid was observed. When the passage of the current was maintained for a very long time, the temperature of the fluid was gradually raised; simultaneously with this the

evolution of gas at the negative pole is increased, as is also the evolution of sulphurous acid, the blue colour disappearing. If the tube be immersed in water gradually increasing in temperature, the last traces of a blue colour disappear at 140° F., at the same time that there is a stronger evolution of sulphurous acid. If the tube be allowed to cool again slowly, the appearance of blue streaks recommences immediately.

A mixture of 2 parts or 1 part of anhydrous acid with 1 part of hydrated acid is still more readily decomposed than the preceding.

From the appearance of the blue fluid at the negative pole, the author concludes that sulphur is separated there; this, as is well known, dissolves with a blue colour in anhydrous sulphuric acid. At the same time oxygen is evolved at the positive pole.

Fusible molybdic acid is also directly decomposed by the current. —Liebig's *Annalen*, cix. p. 129.

On a new Method of forming Chloride of Benzole. *By* M. Beketoff.

A quantity of anhydrous bisulphate of potash and chloride of sodium is allowed to act upon benzoic acid at the temperature of 392° F. Chloride of benzole is thus formed, which, however, remains for the most part in mechanical combination with the mixture from which it has been generated. It may be separated by means of æther. Its formation may be explained by the following equation:—

$$\left.\begin{matrix} C^{14}H^{5}O^{2} \\ H \end{matrix}\right\} O^{2} + S^{2}O^{6} + NaCl = C^{14}H^{5}O^{2}Cl + NaS^{2}O^{8} + HCl.$$

Bullet. de la Soc. Chim. de Paris, Jan. 1859.

On the Action of Air on Mixtures of Sulphide of Calcium and Carbonate of Potash or Soda. *By* J. Pelouze.

On exposing to a dull red heat a sample of artificial crude soda which I suspected to have absorbed moisture and the value of which I wished to ascertain, I obtained a result altogether unexpected. The sample of soda in question ought to have indicated 38° B., or, in other words, to have contained 41 hundredths of its weight of pure carbonate of soda; and in fact, on dissolving out the alkali without previously heating the sample, I found it to mark 38 alkalimetric degrees; but if kept at a red heat for a few minutes only, 5 grms. (77 grs.) of this soda, which is the usual quantity taken for testing, lost sometimes 20, sometimes 30, 40, and 50 per cent. of its strength, and even more if the action of heat was prolonged. I soon discovered the cause of this disappearance of the carbonate of soda.

A few large pieces of crude soda kept at a dull red heat for an hour in an earthen tube, and then lixiviated, gave an abundant crop of crystals of sulphate of soda. In the mother-ley there remained

only a very minute quantity of carbonate of soda, and the residue was composed chiefly of carbonate of lime. When calcined in the air, crude soda increases in weight in proportion to the decrease of its alkalimetric strength. In an atmosphere free from oxygen, in carbonic oxide for example, its weight and strength remain the same. This fact is very easily explained. The sulphide of calcium which crude soda contains in a state of oxysulphide, combines with oxygen, and is converted into sulphate by the double influence of heat and air. When crude soda so heated is lixiviated, an exchange of bases and acids takes place between the carbonate of soda and the sulphate of lime, when sulphate of soda and carbonate of lime are produced. This sulphatization by heating is also produced with the soda-residue and with sulphide of calcium, as is well known; and the presence of carbonate of soda, far from preventing it, seems rather to hasten and favour it.

The decomposition is important in chemical analysis as well as in the manufacture of crude soda. It shows that to ascertain the value of alkaline carbonates, when they are mixed with earthy sulphides, it is necessary to prevent the access of air in drying them, otherwise their strength diminishes and sometimes completely disappears. It is remarkable that analytical experiments upon a substance like soda, which is so much used, should not have shown long before this, the destruction of crude soda by hot air and its rapid return to the primary substances from which it is prepared, viz. sulphate of soda and carbonate of lime. Manufacturers will henceforth know how destructive the combined action of air and heat is to common soda, and the great care which should be taken to guard against their influence. In the soda-furnaces this decomposition does not take place, because the mixture of chalk, sulphate of soda, and charcoal constantly disengages carbonic oxide, and the oxygen of the air which circulates in the apparatus is consumed in converting this into carbonic acid. There is no doubt that if the operation were prolonged, and the combustible gases which protect the soda were replaced by air, the value of the soda would be more or less diminished.

The alteration of the soda is manifested at a temperature much below that of a dull red heat. Thus, if an open tube containing crude soda be exposed in an oil-bath to a temperature of 390°—570° for several hours, a decrease of its alkalimetric strength is easily perceptible. A similar alteration, but in a lesser degree, takes place in crude soda which has been exposed to the air for several months in warehouses; it loses part of its strength, and sulphate of soda is always found in it, the presence of which is explained by the oxidation of a certain quantity of sulphide of calcium. I have already said that a similar decomposition to that of crude soda takes place under similar circumstances wherever alkaline carbonates and earthy sulphides come together. I may mention especially the mixtures of carbonates of potash and soda derived from fermented molasses, which of late years have been so extensively used in manufactures. These salts are often mixed with sulphide

of calcium, and their alkalimetric strength is diminished by several degrees when they are exposed to a red heat; the change, however, is slower and not so great as in the case of crude soda.—*Comptes Rendus*, April 18, 1859.

ANALYTICAL CHEMISTRY.

New Process for determining the Amount of Pure Peroxide of Manganese in the Native Ore. By G. Nolte, *of Clausthal.*

All the methods hitherto employed for determining the amount of pure peroxide of manganese in the native oxide, labour under the common defect of being only applicable in a well-appointed laboratory; as business tests they are mostly too complex. A method which has been contrived by F. C. Fikentscher, suggested by Fuch's iron test, forms an exception; it unites simplicity with sufficient accuracy (as far as ·25 to ·5 per cent.).

The test in question rests on the fact, that for every atom of peroxide the ore contains, it will set free one atom of chlorine from hydrochloric acid, which, in turn, will convert two atoms of copper into dichloride. Strong, chemically pure, hydrochloric acid is poured over a quantity of the native peroxide in a retort, and an excess of copper is added, the evolution of free chlorine being avoided by keeping the retort as cool as possible until the ore is completely decomposed. The mixture is then heated to the boiling-point, so as to convert the protochloride at first formed into dichloride. The loss of copper in weight gives the amount of peroxide in the ore, since every two atoms of copper dissolved answer to one of peroxide.

If the mineral under examination consists, either in part, or altogether, of the hydrated sesquioxide of manganese, it is not enough to keep the retort cool; notwithstanding the utmost caution, chlorine will escape, owing to the rapidity with which the mineral is decomposed, so that the amount of peroxide, when so determined, appears too small. This inconvenience is, however, easily avoided by adding some ferrous salt in such quantities that all the chlorine that is evolved is spent in the further oxidation of the iron, and is therefore unable to escape. The result of the test is thereby in no degree vitiated, since the sesquioxide (or sesquichloride) of iron generated, itself dissolves just as much copper as the chlorine employed in its formation would have done.

It is necessary, however, that the protochlorate of iron employed in this process should be altogether free from sesquichloride, or an excess of peroxide will be shown. A pure protochloride for this purpose is most easily obtained by dissolving a large quantity of iron in hydrochloric acid, and adding, as often as the experiment is required to be repeated, a small quantity of sulphide of iron (or sulphide of ammonium) to the portion of the solution to be employed, and warming the mixture until the smell of sulphuretted hydrogen passes off. No undissolved sulphide of iron must, however, remain,

for which reason it is better for the solution to contain a considerable quantity of free acid.

If the test has to be repeated many times, it is advisable to ascertain the amount of iron contained in the solution (which should be as much as possible), so that the exact quantity required may be measured out. An excess of iron solution does not, however, affect the accuracy of the test.

The process is conducted in the following manner:—

Instead of weighing out a test hundredweight, from which the quantity of peroxide would afterwards require to be calculated, a weight of $68\frac{3}{4}$ pounds of the ore is taken, having been first well dried, or containing a known amount of water.

This quantity of ore, if it consisted of chemically pure peroxide, would dissolve precisely 100 parts of copper, since $MnO^2 : 2Cu = 544{\cdot}4 : 792{\cdot}0 = 68{\cdot}74 : 100$.

A calculation is in this manner avoided, since the number of pounds which the copper is found to have lost when the process is concluded, is precisely the per-centage of peroxide in the ore.

The native oxide under examination is placed in a glass retort, and covered with the solution of protochloride of iron, which may be added while still warm. As much of this solution is taken as would contain from 92 to 95 pounds of iron. To this a known weight (about 2 cwts.) of copper is added in the form of small twisted, but very clean shavings, and then some hydrochloric acid.

The retort is then placed on a sand-bath, and the liquid is boiled until the dark brown solution becomes clear yellow or greenish, and no longer changes colour. The decomposition of the ore hardly lasts a minute, while formerly two or three hours were required, the oxidation of the dichloride of copper through access of atmospheric air being consequently much more probable than in the method now described.

If the solution boils away too rapidly during the process, so as to leave the copper no longer completely covered, or if the dichloride of copper separates out, so as to cause the liquid to boil irregularly, hot concentrated hydrochloric acid may be added.

After boiling for about half an hour the decomposition is completed. The retort is then removed from the sand-bath and filled with cold deaërated water. The liquid, which has become milky through the separation of the dichloride of copper, is decanted off, and the copper left is rinsed briskly in cold water; the dark powder adhering to its surface (carbon) being wiped away with a small rag. It is then at once placed to dry on a sand-bath, and afterwards weighed.

It is seldom that the ore under examination is entirely free from oxide of iron. As this affects the result of the process, without however assisting in the evolution of the chlorine, the quantity of copper which in the principal process was taken up by this oxide must be ascertained by a separate experiment. For this purpose the same quantity of the ore as before is boiled in hydrochloric acid until the evolution of chlorine is completed; some copper sheeting

(from 50 to 100 pounds) is then added, and the process conducted as before. A variable loss of copper, depending on the amount of iron present, ensues, from which the latter can be calculated. If the amount of copper so lost be subtracted from that lost in the principal process, the difference in pounds will be the amount per cent. of pure peroxide in the ore. If, for example, the first process gives a loss of 78 pounds of copper, and the second of 6 pounds, the ore contains 78—6=72 per cent. of peroxide.

Tests made for the purpose of comparison in the foregoing manner, gave not only very small differences as between themselves (not $\frac{1}{4}$ per cent.), but also almost exactly the same result as Fresenius and Will's process. The fact that the latter indicated the presence of $\frac{1}{2}$ per cent. more peroxide, may perhaps have resulted from the ore under examination having contained traces of carbonates, causing the result to appear too high.—*Berg- und Hüttemänn Zeitung*, 1859, No. 17.

Protochloride of Palladium, an excellent reagent for various Gases. *By* Professor Böttger.

If it be required to ascertain the presence of small quantities of coal-gas, carbonic oxide, marsh-gas, elayle gas, or hydrogen gas, in a space in which we may suppose one or other of these gases to exist, a solution of protochloride of palladium, as free as possible from acid, is found to be an excellent test for this purpose. In an atmosphere of coal-gas, which, as is well known, is a mixture of the most various gases, such as carbonic oxide, hydrogen, marsh-gas, elayle gas, and many other carburets of hydrogen, a strip of linen or cotton stuff, soaked in a moderately concentrated solution of protochloride of palladium, and half-dried by slight pressure between blotting-paper, will be seen to acquire an intense black colour within a few minutes. Exactly the same thing occurs, and even in a comparatively shorter time, when a strip of this kind is dipped into an atmosphere of carbonic oxide; marsh-gas, elayle gas, and hydrogen gas have the same action.

As a contribution to a very instructive class experiment, the following process appears to be peculiarly adapted. A strip of linen, moistened as above with protochloride of palladium, is firmly fixed in the tubulure of a bell-glass, of any size, by means of a split cork; the bell-glass is then placed upon a plate, upon the bottom of which any bad conductor of heat, such as a wooden disc or the like, is placed; if a fragment of glowing wood-coal be then rapidly introduced under the bell-glass and laid upon the wooden disc, the strip of linen is seen in a few moments to acquire an intensely black colour in this atmosphere of carbonic oxide gas.

If a small glass cylinder, very slightly moistened internally with solution of protochloride of palladium, be held over an open gas-burner, the inner wall of the cylinder rapidly becomes coated with a thin black film of metallic palladium. If a current of chemically pure hydrogen be passed through a cylindrical glass, filled with

dilute solution of protochloride of palladium, a considerable time (about ten minutes) passes before any visible reaction, such as turbidity or blackening of the fluid, usually occurs; but it always does take place, and after the action has continued for a long time, we may even see a deep black flocculent body separate in abundance, which consists of very finely divided palladium, and which, when dried and calcined, is converted without loss of weight into the gray spongy modification, whilst the inner wall of the glass becomes at the same time coated with a specular metallic coat. In a similar way, but in a far higher degree than by pure hydrogen gas, the solution is acted upon by elayle gas and marsh-gas, but is not in the least altered by carbonic acid, oxygen, nitrogen and sulphurous acid gases. Considering the facility with which the decomposition of protochloride of palladium is effected by the above-mentioned gases, this solution stands quite alone. That its reduction by the different gases takes place in a longer or shorter time, appears to depend in part upon the unequal solubilities of the gases in water. —*Jahresber. des Physikal., Vereins in Frankfurt a. M.* 1857—1858; Dingler's *Polyt. Journal*, clii. p. 76.

Note on the Cause of the Formation of Carbonic Oxide Gas in the Volumetric determination of Nitrogen. By A. Schrötter.

Limpricht stated some time since, that metallic copper is capable of reducing carbonic acid to the state of carbonic oxide, and that an error in the determination of nitrogen may arise from this.

The author also frequently observed, that when the copper is heated gas-bubbles again appear, which are not absorbed by potash, although the atmospheric air had been previously almost entirely expelled from the combustion tube. Melsens likewise observed nearly the same phænomena long ago, so that there can be no doubt as to the accuracy of the fact.

The author supposed that the reduction of the carbonic acid was produced, not by the copper, but by the hydrogen mixed with it.

He conducted dry carbonic acid slowly through a hard combustion tube, wrapped in sheet-iron, and filled with bright, thin strips of copper, such as may be obtained by flattening copper wire, which may be in all cases advantageously substituted for copper turnings. The length of the layer of copper amounted to 50 centims.; and it was heated as strongly as could be done with a furnace for organic analysis with unobstructed draught and constant fanning. The heating was commenced as soon as the apparatus was entirely filled with carbonic acid. The gas passing through was for the most part absorbed by potash, and the small quantity left unabsorbed was nothing but nitrogen gas, derived, no doubt, from the atmospheric air which still remained in the apparatus.

This experiment shows unmistakeably that pure copper, which has not previously been in contact with hydrogen, cannot decompose carbonic acid when heated to redness.

Fine copper turnings, previously cleaned, were then heated for a

time in oxygen gas, until they were to a certain extent (but not completely) converted into oxide of copper. They were then reduced, in the same tube, by means of hydrogen gas; and lastly, after the cooling of the apparatus, a current of dry atmospheric air, which had previously passed through a tube filled with cotton, was allowed to pass through the tube for half an hour. These copper turnings were now, as before, strongly heated in carbonic acid, after nearly all atmospheric air had been expelled from the tube. But in this case also no carbonic oxide gas was obtained, but only a very small quantity of nitrogen. In this case, therefore, the carbonic acid remained undecomposed.

It now only remained to reduce laminar oxide of copper with hydrogen, and after it had cooled therein to conduct carbonic acid through the tube, and then to heat it. Under these circumstances, carbonic oxide gas was obtained exactly as stated by Limpricht. From these experiments it appears therefore—

1. That carbonic acid is reduced to carbonic oxide by hydrogen, even at a low red heat.

2. That pure metallic copper, not previously in contact with hydrogen, cannot decompose carbonic acid even at a strong red heat.

3. That the evolution of carbonic acid, observed by Limpricht, arises solely from the reducing action of hydrogen upon carbonic acid; hydrogen, as has already frequently been observed, adhering obstinately to the metal.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xxxiv. p. 27.

Simple Method of distinguishing Citric and Tartaric Acid. *By* M. Barbet.

On a glass plate strew the crystals to be examined over a thin stratum of a weak solution of caustic potash. After a few seconds of contact, crystals of tartaric acid become white and opake, and at last separate into microscopic crystalline particles. The crystals of citric acid, on the contrary, remain transparent, and partly dissolve in the alkaline fluid. The difference is so striking, that even the quantity of the one or the other acid can be approximately estimated.

This method may still be applied when the acids in question are pulverized, only in this case the experiment must be performed on the object-glass of a microscope.—*Journ. de Med. de Bord.*; *Archiv der Pharmacie*, cxlviii. p. 216.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On Tungsten Steel. *By* F. X. Wurm.

Franz Mayr has produced, at his cast-steel works at Kapfenberg in Styria, cast steel of such dimensions, forms, and excellent

quality, as could previously only be obtained from Krupp of Essen. Oblique cog-wheels for coining machines and locomotives, axles for railway carriages, boiler plates, angle knees, and round, flat, and quadrangular rods, of various sections, have now been produced by Mayr for more than a year.

What particularly deserves to be mentioned with regard to these articles, is Mayr's unrivalled tungsten-steel distinguished by the fineness of its crystalline texture and its remarkable hardness, so much so, indeed, that the experiments made with it several months ago have shown that tools made from it for cutting toothed wheels, borers, chisels, punches, turning tools, planing blades, &c., retain their power of cutting four times as long as those made of Hundsman-steel previously regarded as the best. This steel may therefore be recommended as the best for these purposes.

Tungsten has nearly the same specific gravity as gold, and this density is recognizable in the cast steel alloyed with it, by the alteration in the grain of the fractured surface, and by the heigthened ring of the steel.

In hardness, metallic tungsten nearly approaches the hardest of natural bodies, and it communicates this property to cast steel, without injuring its tenacity and malleability when the addition is of 2—5 per cent.

The absolute solidity of tungsten-steel exceeds that of all other known steels, for fifteen consecutive experiments with a machine in the Polytechnic Institute of Vienna showed the highest power of resistance to be 1393 hundredweights, and the lowest 1015 hundredweights, giving an average of $1158\frac{13}{15}$ hundredweights to the square inch; so that this steel exceeds all other kinds hitherto tried.

The ore of tungsten from which the metal is obtained, usually occurs in company with tin-stone; it has probably hitherto never obtained any technical application, as it has only been regarded as a mineralogical curiosity.

More recent investigations have shown, however, that the arts may derive considerable benefit from it. One of the richest sources of this ore is possessed by the Austrian empire in the tin mines of Zinnwald in Bohemia, where the tungsten ore has been thrown upon the heaps as worthless for nearly five hundred years.

Mayr has the great merit of having been the first to bring this new and hitherto unemployed metal into use in the manufacture of cast steel on the large scale, having introduced tungstic cast steel into commerce of the most various degrees of hardness, and of any dimensions.

The price of this steel, notwithstanding its remarkable goodness, is lower than that of the English cast steel, over which the uniformity of its crystalline texture gives it a peculiar advantage.

The above properties of density, hardness, and strength are also communicated by tungsten to cast iron, and this alloy may probably be useful for crushing-rollers, and may perhaps in time attract the attention of the artillery.—Dingler's *Polyt. Journal*, clii. p. 178.

PROCEEDINGS OF SOCIETIES.

Royal Society.

March 31, 1859. (Sir Benjamin C. Brodie, Bart., Pres., in the Chair.)

"On the Oxidation of Glycol, and on some Salts of Glyoxylic Acid." By H. Debus, Ph.D.

If glycol be oxidized with nitric acid, according to Wurtz*, it is converted into glycolic and oxalic acids.

$$\underbrace{C_2H_6O_2}_{\text{Glycol.}} + O_2 = \underbrace{C_2H_4O_3}_{\text{Glycolic acid.}} + \underbrace{H_2O}_{\text{Water.}}$$

$$\underbrace{C_2H_6O_2}_{\text{Glycol.}} + O_4 = \underbrace{C_2H_2O_4}_{\text{Oxalic acid.}} + \underbrace{2H_2O}_{\text{Water.}}\dagger$$

As the formation of these acids from glycol is analogous to the production of acetic acid from ethylic alcohol, it may be assumed that the bibasic oxalic acid stands to the biatomic glycol in the same relation as the fatty acids do to their corresponding alcohols. Alcohol is not converted at once into acetic acid, an intermediate substance—aldehyde—being formed. The formation of a similar body from glycol is highly probable. If two or four atoms of hydrogen be removed from glycol, an aldehyde of the composition of acetic acid or of the formula $C_2H_2O_2$ may be produced. Glyoxal, obtained by the oxidation of ethylic alcohol, has indeed the composition corresponding to the above formula and the characteristic properties of an aldehyde. Nitric acid converts it rapidly into oxalic acid. Consequently glycol, glyoxal, and oxalic acid bear a similar relation to each other as ethylic alcohol, aldehyde, and acetic do.

$\underbrace{C_2H_6O}_{\text{Alcohol.}}$	$\underbrace{C_2H_4O}_{\text{Aldehyde.}}$	$\underbrace{C_2H_4O_2}_{\text{Acetic acid.}}$
$\underbrace{C_2H_6O_2}_{\text{Glycol.}}$	$\underbrace{C_2H_2O_2}_{\text{Glyoxal.}}$	$\underbrace{C_2H_2O_4}_{\text{Oxalic acid.}}$

Another connexion between glycol and glyoxal is that they both produce glycolic acid, the former by oxidation, and the latter by combination with one atom of water. I treated glycol, which was diluted with water, with fuming nitric acid at about 30° C., and evaporated the acid liquid, as soon as the action was completed, on the water-bath until it assumed the consistency of syrup‡. This residue was found to contain, as previously shown by Wurtz, oxalic and glycolic acids; but I also found therein glyoxylic acid and a body which comported itself with some reagents like glyoxal. Want of material, however, prevented its being identified with the latter.

Before I proceed to make some observations on these facts, I shall first mention a few salts of glyoxylic acid not yet described.

* Comp. Rend. xliv. 1306. † C = 12, H = 1, O = 16.

‡ "On the Action of Nitric Acid on Alcohol," Phil. Mag. Jan. 1857; Ann. der Chem. und Pharm. cii. 26.

Glyoxylate of silver, $C_2HAgO_3+H_2O$,

is obtained as a white crystalline powder when nitrate of silver is precipitated with glyoxylate of ammonia. This salt is but slightly soluble in cold water, and is decomposed by light with great rapidity.

Glyoxylate of baryta, $C_2HBaO_3+2H_2O$.

Diluted glyoxylic acid is digested at common temperatures with carbonate of baryta until the acid is completely neutralized, and the filtered solution evaporated *in vacuo*. As soon as the liquid has arrived at a certain degree of concentration, small white crystals of glyoxylate of baryta begin to separate. This compound is partially decomposed into oxalate of baryta and glycolic acid if it be heated to 120° C., or if the temperature of its watery solution be raised to the boiling-point. With nitrate of silver, acetate of lead, and lime-water, it comports itself like glyoxylate of lime.

Glyoxylate of zinc, $C_2Zn_2O_3+2H_2O$,

is produced as a white crystalline precipitate when a strong solution of glyoxylate of lime is precipitated with acetate of zinc. This compound is slightly soluble in water, but is easily dissolved by acetic and hydrochloric acids and by caustic potash. The two atoms of water cannot be removed without decomposing the salt.

Glyoxylate of ammonia, $C_2H(NH_4)O_3$.

This compound was prepared by precipitating glyoxylate of lime with its equivalent quantity of oxalate of ammonia, and evaporating the filtrate from the oxalate of lime over sulphuric acid *in vacuo*. The glyoxylate of ammonia is obtained in small, prismatic and colourless crystals, which dissolve easily in water. The concentrated solution turns yellow when it is boiled, or evaporated at 100° C. It produces with nitrate of silver and acetate of lead crystalline precipitates at once, but with sulphate of copper only after the lapse of some time. Solution of caustic potash, mixed with it, causes the evolution of ammonia even at common temperatures.

According to the composition of glyoxylate of ammonia, the formula of glyoxylic acid is $C_2H_2O_3$*. It is worthy of notice, that the other salts of this acid which have been examined, contain one or two atoms of water which cannot be expelled without decomposing the compound.

Glyoxal is oxidized, by treatment with dilute nitric acid, into oxalic acid, and as an intermediate substance glyoxylic acid is formed.

$C_2H_2O_2$ = Glyoxal.
$C_2H_2O_3$ = Glyoxylic acid.
$C_2H_2O_4$ = Oxalic acid.

Glyoxal has not been proved with certainty to be one of the products of the oxidation of glycol; nevertheless its formation from this alcohol may be foreseen with great probability, as it stands to glyoxylic and oxalic acids, both of which are formed by the oxidation of

* "On Glyoxal," Phil. Mag. Jan. 1857; Ann. der Chem. und Pharm. cii. 29.

glycol, as ethylic aldehyde does to acetic acid. The relation of glyoxylic to oxalic acid is like that of sulphurous to sulphuric acid.

$\underbrace{C_2H_2O_3}$ $\underbrace{SH_2O_3}$

Glyoxylic acid. Sulphurous acid.

$\underbrace{C_2H_2O_4}$ $\underbrace{SH_2O_4}$

Oxalic acid. Sulphuric acid.

Glyoxylic acid resembles in many respects formic acid. Concentrated sulphuric acid separates from the salts of formic acid carbonic oxide, whilst it combines with the rest of the constituents. Glyoxylate of lime dissolves in an excess of sulphuric acid, and the solution evolves at a temperature of from 40° to 50° C., without blackening, pure carbonic oxide. At the end of the experiment, and when the temperature of the liquid is raised, a little sulphurous acid makes its appearance.

Relying on Berthelot's experiments, formic acid we can conceive to be formed by the addition of the molecule carbonyle to the type water. In the same manner glyoxylic acid might be produced by adding oxalyle to one atom of water.

$$CO + H_2O = \underbrace{CH_2O_2}$$

Formic acid.

$$C_2O_2 + H_2O = \underbrace{C_2H_2O_3}$$

Glyoxylic acid.

Since both acids are easily oxidized, the one to carbonic, and the other to oxalic acid, we may say that, with regard to composition, formic acid stands to carbonic acid in a similar relation as glyoxylic acid does to oxalic acid.

$CO+H_2O=\underbrace{CH_2O_2}$ $C_2O_2+H_2O=\underbrace{C_2H_2O_3}$

Formic acid. Glyoxylic acid.

$CO+H_2O_2=\underbrace{CH_2O_3}$ $C_2O_2+H_2O_2=\underbrace{C_2H_2O_4}$

Carbonic acid plus water. Oxalic acid.

But with regard to other properties, these acids do not correspond to each other: thus formic acid is monobasic and carbonic acid bibasic, whilst both glyoxylic and oxalic acids are biatomic. Further, the latter two are derived from the same alcohol, which is not the case with carbonic and formic acids. Amongst the products of the oxidation of glycol occurs also glycolic acid, which is produced from glyoxal by the assimilation of water.

$$\underbrace{C_2H_2O_2} + H_2O = \underbrace{C_2H_4O_3}$$

Glyoxal. Glycolic acid.

Some regard glycolic acid ($C_2H_4O_3$) as a bibasic acid. According to this view, it would stand to glycol as acetic acid does to common alcohol.

$$\underbrace{C_2 H_6 O_2}_{\text{Glycol.}} \qquad \underbrace{C_2 H_6 O}_{\text{Alcohol.}}$$

$$\underbrace{C_2 H_4 O_3}_{\text{Glycolic acid.}} \qquad \underbrace{C_2 H_4 O_2}_{\text{Acetic acid.}}$$

But with this view the capacity of saturation of glycolic acid does not agree. For according to our present experience, if we adopt the formula $C_2 H_4 O_3$, it evidently combines only with one atom of base. Before we have discovered compounds represented by the general expression $C_2 H_2 M_2 O_3$, I think we are not justified in placing glycolic acid in the same relation to glycol as we do acetic acid to common alcohol. According to our present knowledge, this position must be assigned to oxalic acid.

We can represent to our minds the derivation of glycolic acid from acetic acid in the following manner. If in acetic acid one atom of hydrogen be replaced by peroxide of hydrogen, we obtain a body which has the composition of glycolic acid.

$C_2 H_4 O_2$ = acetic acid.
$C_2 H_3 (HO) O_2$ = glycolic acid.

But, according to the following observations, this view appears not to be correct; for glycolic acid can be formed from glycolide and water, and probably also again can be resolved into these two substances in the same way as lactide and water by their union produce lactic acid, and the decomposition of the latter by heat yields lactide again. If, therefore, peroxide of hydrogen be contained in glycolic acid, it must be present in glycolide.

If monochlorinated acetate of potash be decomposed, according to Kekulé, glycolic acid and glycolide are formed. The formation of the latter precedes that of the glycolic acid; but if the monochlorinated acetate of potash could be obtained anhydrous, no doubt only glycolide would result from its decomposition. The monochlorinated acetate of potash can be represented as consisting of three parts,—of potassium, of oxygen, and of chlorinated acetyle.

$$\left.\begin{matrix} C_2 H_2 ClO \\ K \end{matrix}\right\} O.$$

At a higher temperature chlorine and potassium form chloride of potassium. After the removal of the chlorine, the chlorinated acetyle is converted into the biatomic radical $C_2 H_2 O$, which unites with one atom of oxygen, and forms glycolide.

$$\left.\begin{matrix} \overbrace{C_2 H_2 OCl} \\ | \\ K \end{matrix}\right\} O$$

According to its formation, the glycolide cannot contain any peroxide of hydrogen, and consequently it appears that also glycolic acid cannot be considered as acetic acid wherein one atom of hydrogen has been replaced by peroxide of hydrogen.

I beg to conclude with an empirical derivation of several of the compounds mentioned from hydruret of ethyle.

$C_2H_2H_2H_2$ = Hydruret of ethyle.
$C_2H_2H_2O$ = Aldehyde.
C_2H_2OO = Glyoxal and glycolide.
C_2OOO = Anhydrous oxalic acid.
$C_2H_2H_2H_2+O$ = Alcohol.
$C_2H_2H_2O+O$ = Acetic acid.
C_2H_2OO+O = Glyoxylic acid.
C_2OOO+O = Carbonic acid.
$C_2H_2H_2H_2+H_2O=C_2H_8O$.
$C_2H_2H_2O+H_2O$ = Glycol.
$C_2H_2OO+H_2O$ = Glycolic acid.
C_2OOO+H_2O = Oxalic acid.

April 14, 1859. (Sir Benjamin C. Brodie, Bart., Pres., in the Chair.)

"On the Action of Acids on Glycol." By Dr. Maxwell Simpson.

The glycol employed in the following research was prepared according to Dr. Atkinson's excellent method *, to whom is due the credit of having first substituted acetate of potash for acetate of silver in its preparation. He was not the first, however, to prepare it from bromide of ethylene, as M. Wurtz has been in the habit of preparing it from that body for the last two years.

The following slight modification of Dr. Atkinson's method will be found very convenient. Instead of heating the materials for forming the monoacetate of glycol in a close vessel, they are heated in a large balloon, connected with a Liebig's condenser in such a manner as to cause the condensed vapours to flow back into the balloon.

Action of Sulphuric Acid on Glycol—Sulphoglycolate of Baryta.—Sulphuric acid forms an acid ether with glycol, which gives a soluble salt with baryta. This compound is readily prepared by exposing a mixture of equivalent quantities of glycol and sulphuric acid ($S_2H_2O_8$) to the temperature of 150° Cent., diluting with water and neutralizing with carbonate of baryta. This liquid, on being filtered, and evaporated on a water-bath to the consistence of a syrup, gives on cooling a white solid mass, which is the body in question. This was pressed between folds of blotting-paper, dried *in vacuo* over sulphuric acid, and analysed. The numbers obtained on analysis lead to the formula $\left.\begin{matrix}C_4H_5O_2\\S_2O_4\\Ba\end{matrix}\right\}O_4$,

as will be seen from the following per-centage Table:—

	Theory.		Experiment.			
			I.	II.	III.	IV.
C_4	24·00	11·45	10·71†	——	——	——
H_5	5·00	2·40	2·79	——	——	——
S_2O_8	80·00	38·15	——	38·09	——	——
BaO	76·50	36·51	——	——	36·50	36·10
O_3	24·00	11·49	——	——	——	——
	209·5	109·00				

* Philosophical Magazine, Dec. 1858.

† Chromate of lead was employed in this analysis.

The formation of this compound may be thus explained :—

$$\left.\begin{matrix} C_4H_4 \\ H_2 \end{matrix}\right\} O_4 + S_2H_2O_8 = \left.\begin{matrix} C_4H_5O_2 \\ S_2O_4 \\ H \end{matrix}\right\} O_4 + H_2O_2.$$

On neutralizing this compound with carbonate of baryta, the basic hydrogen is replaced by one atom of barium. I propose to call this salt sulphoglycolate of baryta. It is analogous in composition to the sulphoglycerate of baryta obtained by M. Pelouze. This salt does not readily crystallize. It is almost insoluble in ether and in absolute alcohol, but freely soluble in water. It is somewhat deliquescent. Exposure to the temperature of 100° Cent. causes slight decomposition. From its solution in water, sulphuric acid precipitates sulphate of barytes. Baryta-water occasions no precipitate, at least in the cold; on heating, however, for some time, it becomes turbid, from the separation of the same salt.

Action of Hydrochloric and Acetic Acids on Glycol—Chloracetine of Glycol.—A mixture of equivalent quantities of glycol and glacial acetic acid was introduced into a long tube and saturated with dry hydrochloric acid. The tube was then hermetically sealed, and exposed to the temperature of a water-bath for about four hours. On opening the tube and adding water to its contents, a heavy oil separated, which was well washed with the water, in order to remove any acetic acid or undecomposed glycol it might contain, dried over chloride of calcium, and distilled. Almost the entire quantity passed over between 144° and 146°. Specimens obtained at different times gave the following numbers on analysis, which lead to the formula

$$\left.\begin{matrix} C_4H_4 \\ C_4H_3O_2 \\ Cl \end{matrix}\right\} O_2.$$

C_8	48·00	39·18	38·96	38·98	——
H_7	7·00	5·71	6·05	5·99	——
O_4	32·00	26·14	——	——	——
Cl	35·50	28·97	——	——	27·48*
	122·50	100·00			

I propose to call this body chloracetine of glycol. It is the intermediate compound between Dutch liquid and diacetate of glycol. Its formation may be thus explained :—

$$\left.\begin{matrix} C_4H_4 \\ H_2 \end{matrix}\right\} O_4 + \left.\begin{matrix} C_4H_3O_2 \\ H \end{matrix}\right\} O_2 + HCl = \left.\begin{matrix} C_4H_4 \\ C_4H_3O_2 \\ Cl \end{matrix}\right\} O_2 + 4HO.$$

Chloracetine of glycol is a colourless liquid, heavier than water, its specific gravity being 1·1783 at 0° Cent. It boils at 145°, distilling without decomposition. It is not decomposed by cold water, at least not to any great extent; even boiling water effects its decom-

* A slight loss occurred in this analysis.

position with difficulty. Heated with potash, it gives chloride of potassium and acetate of potash. It is probable that the ether of glycol is also formed in this reaction, or perhaps glycol itself. This point I have not yet been able to determine. Chloracetine is isomeric with a compound I obtained a short time ago, by exposing ordinary aldehyde to the action of chloride of acetyle ($C_4 H_3 O_2 Cl$)*. This body differs from the chloracetine in its boiling-point, which is about 23 degrees lower, and in being more readily decomposed both by water and potash. The products formed by the action of potash also establish a difference between these bodies. Both give chloride of potassium and acetate of potash, but the body from aldehyde gives, in addition, resin of aldehyde; whereas from chloracetine no resin could be obtained. Chloracetine has since been prepared by M. Lorenzo in a manner analogous to that by which I prepared its isomer, namely, by treating glycol with chloride of acetyle. These compounds find their places in two very remarkable series of isomeric bodies, proceeding from ethylene (olefiant gas) and ethylidine ($C_4 H_4$?), supposed to be contained in the chloride of ethylidine derived from aldehyde. The following is a list of these compounds:—

	Ethylidine.	Ethylene (olefiant gas).	
	$C_4 H_4$ (?)	$C_4 H_4$	
Aldehyde . .	$C_4 H_4 O_2$	$C_4 H_4 O_2$	Oxide of ethylene. Ether of glycol (Wurtz).
Chloride of ethylidine . (Wurtz)	$C_4 H_4 Cl_2$	$C_4 H_4 Cl_2$	Dutch liquid.
Geuther . .	$\left.\begin{matrix} C_4 H_4 \\ C_4 H_3 O_2 \\ C_4 H_3 O_2 \end{matrix}\right\} O_4$	$\left.\begin{matrix} C_4 H_4 \\ C_4 H_3 O_2 \\ C_4 H_3 O_2 \end{matrix}\right\} O_4$	Diacetate of glycol (Wurtz).
Chloracetine of ethylidine (Simpson)	$\left.\begin{matrix} C_4 H_4 \\ C_4 H_3 O_2 \end{matrix}\right\} O_2$ Cl	$\left.\begin{matrix} C_4 H_4 \\ C_4 H_3 O_2 \end{matrix}\right\} O_2$ Cl	Chloracetine of glycol (Simpson).
(Wurtz and Frapolli)	$\left.\begin{matrix} C_4 H_4 \\ C_4 H_5 \end{matrix}\right\} O_2$ Cl	$\left.\begin{matrix} C_4 H_4 \\ C_4 H_5 \end{matrix}\right\} O_2$ Cl	Not yet discovered.
Acetal (Döbereiner)	$\left.\begin{matrix} C_4 H_4 \\ (C_4 H_5)^2 \end{matrix}\right\} O_4$	$\left.\begin{matrix} C_4 H_4 \\ (C_4 H_5)^2 \end{matrix}\right\} O_4$	Diethyl-glycol (Wurtz).

I am still studying the action of acids on glycol, and hope soon to be able to communicate further results.

* Comptes Rendus, 29 Nov. 1858.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Mercurial Bases. By Dr. Otto Schmieder.

The compound which is obtained when oxide of mercury is brought in contact with ammonia was first investigated by Guibourt, who regarded it as a direct compound of these two bodies, and supposed that its constitution was such that the hydrogen of the ammonia was exactly sufficient to convert the oxygen of the oxide into water. Subsequent investigations by Thenard, Fourcroy, Hennel, and Mitscherlich led to the supposition that the bodies produced by the action of ammonia upon the salts of mercury were also to be regarded as compounds of oxide of mercury with ammonia. According to this view oxide of mercury and ammonia is $=3\,HgO + NH^3 + 2\,Aq$, and white precipitate (Mitscherlich) $=2\,HgO + NH^4\,Cl$.

Kane, in accordance with his amide-theory, assumed in these ammoniacal compounds the presence of his hypothetical radical amide or amidogen, NH^2, which he considered to possess the property of forming direct compounds with mercury. In this view the white precipitate does not consist of a compound of oxide of mercury and muriate of ammonia; Kane showed rather that it contained neither oxide of mercury nor water, but was to be regarded as a compound of perchloride of mercury and amidide of mercury, $HgNH^2 + HgCl$. In the same way, according to this theory, the direct compound of oxide of mercury and ammonia is $=HgNH^2 + 3HgO$, the yellow product of the decomposition of white precipitate $= HgNH^2 + HgCl + 2\,HgO$, and ammonia-turpeth $= HgNH^2 + 3\,HgO + SO^3$.

According to Millon's view, the body produced by the action of ammonia upon oxide of mercury behaves as a strong base, furnishes constant compounds with acids, and sets ammonia free from its salts.

In accordance with the amide-theory, it is to be regarded as a compound of amidide of mercury with 3 atoms of oxide of mercury; it is precipitated without decomposition from its salts by the caustic alkalies, when the fluid is not heated to boiling; the base then remains in a hydrated state in the form of a yellow precipitate. In accordance with this view, Millon altered the formulæ proposed by Kane in the following way:—oxide of mercury and ammonia $=3\,HgO, HgNH^2$; the yellow powder from white precipitate $= 2\,HgO, HgCl + HgNH^2$; ammonia-turpeth $= 3\,HgO, HgNH^2 + SO^3$.

Schrötter regards the amide compounds of mercury as multiples of proto- or peroxide and proto- or perchloride of mercury in which one or more equivalents of oxygen or chlorine are replaced by amidogen; and lastly, Hirzel arrived at the conclusion that nitruret of mercury, which has been prepared in an isolated state, may be assumed to exist in these compounds with more reason than the hypothetical amidide of mercury, as in his opinion all the nitrogen cannot be extracted from these compounds by boiling with potash. His formulæ are,—oxide of mercury and ammonia $= Hg^3\,N + HgO + 2\,HO$; white precipitate $= (Hg^3\,N + HgCl) + H^2\,N, HCl$; the yellow powder $= Hg^3\,N + HgCl + 2\,HO$; ammonia-turpeth $= Hg^3N + HgOSO^3 + 2\,HO$.

The investigations of Hofmann and Wurtz led to the extension to these compounds of the ammonium theory, by the assumption that the hydrogen of ammonium or oxide of ammonium may be partially or wholly replaced by mercury. In accordance with this view the following mercurammonium-radicals may be established:—

Mercurammonium	$N\left\{\begin{matrix}Hg\\H^3\end{matrix}\right.$
Bimercurammonium	$N\left\{\begin{matrix}Hg^2\\H^2\end{matrix}\right.$
Trimercurammonium	$N\left\{\begin{matrix}Hg^3\\H\end{matrix}\right.$
Tetramercurammonium	$N\ Hg^4$.

According to this theory, white precipitate would be the chloride of bimercurammonium $= N\left\{\begin{matrix}Hg^2\\H^2\end{matrix}\right. Cl$. As yet we are only acquainted with compounds of the above compounds with halogens, no oxysalts of them having been prepared. It is the object of the present memoir to describe a double salt of sulphate of bimercurammonium with sulphate of ammonia, in which the oxide of bimercurammonium exists as such, together with a series of basic compounds obtained therefrom. By this means the author hopes to furnish a proof that the interpretation by the ammonium-theory is the simplest and least forced, and that the so-called mercuramine-compounds are nothing more than ordinary basic compounds of oxide of mercury with a salt of bimercurammonium.

Double Salt of Sulphate of Bimercurammonium with Sulphate of Ammonia.—The preparation of this salt depends on the well-known property of sulphate of ammonia of dissolving peroxide of mercury in large quantity; the only thing necessary is, that no heat at all should be applied, and the moment must be exactly observed when the oxide of mercury is present in excess, and there is consequently no more free ammonia. The author prepared his sulphate of ammonia by neutralizing pure ammonia with pure sulphuric acid, evaporating the solution in the water-bath with frequent additions of ammonia and crystallizing it; the peroxide of mercury was always employed in the yellow amorphous modification, which was prepared by pouring a solution of bichloride of mercury into a chemically pure solution of potash, and carefully washing the precipitate formed.

In introducing the finely powdered oxide of mercury into the saturated solution of neutral sulphate of ammonia, care must be taken only to add the former in small quantities, and not to add a new portion until the preceding one is completely dissolved. This is continued until the fluid begins to grow turbid, which is caused by the deposition of a white basic compound. If the red modification of peroxide of mercury be employed in place of the yellow one, the reaction is less violent, the sulphate of ammonia dissolves less of it, and the basic salt separates earlier, before the solution is saturated with oxide of mercury. The concentration of the clear solution was effected either by spontaneous evaporation or under the air-pump. In the latter case very delicate, microscopic, acicular crystals were obtained within 24 hours, whilst in the former crystals were only produced in the course of several weeks; but these were larger and of a more normal habit, showing distinctly that they belong to the orthorhombic system, and are partially tabular, like the ordinary form of sulphite of baryta, and limpid; in the fresh state they possess a brilliant glassy lustre, which, however, they lose when long exposed to air and light, but without actually being decomposed. The salt loses water, falls to pieces, and deposits a white basic compound. It dissolves readily in sulphate and muriate of ammonia, and also in dilute and concentrated muriatic acid, and in very dilute sulphuric acid, but is insoluble in concentrated nitric acid. By boiling with concentrated sulphuric acid it is decomposed, persulphate of mercury and sulphate of ammonia being formed. Treatment with dilute solution of potash at the ordinary temperature causes the evolution of ammonia, and the formation of a white basic compound of different composition from that produced by water; if the salt be boiled with concentrated solution of potash, a yellowish compound is first of all formed, and this, when boiled for a long time with fresh solution of potash, is completely decomposed with evolution of ammonia, leaving peroxide of mercury as a residue. Sulphuretted hydrogen produces sulphuret of mercury and neutral sulphate of ammonia. When dried at 194° F., the salt remains white; at 239° F., it becomes slightly reddish, but only loses water. When heated in a glass tube, water

first escapes, then ammonia, and a yellow mass, becoming white on cooling, is sublimed, whilst a speculum of mercury is formed on the walls of the tube. A reddish-brown mass remains, which fuses with strong effervescence with a slight noise and with evolution of sulphurous acid, and leaves no residue when heated to redness.

For analysis, the hydrated salt, completely air-dried, was dissolved in muriatic acid, the mercury was precipitated from the boiling solution by washed sulphuretted hydrogen, and the filtrate employed either to determine the sulphuric acid by precipitation with chloride of barium, or for the determination of the sulphate of ammonia by evaporation in the water-bath; in the latter solution the amount of nitrogen was ascertained by precipitation with perchloride of platinum. The analysis gave—

	I.	II.	III.	IV.	V.	VI.
Mercury	57·3696	57·3795	57·4503	57·2595	57·3682	57·6250
Sulphuric acid	23·4780	23·0158	23·0224	23·0552		
Nitrogen	...	...	...	8·0760	7·9857	8·0455

	Average.		Calculated.
Mercury	57·4086	2	57·4712
Sulphuric acid	23·1178	2	22·9885
Nitrogen	8·0357	2	8·0459
Hydrogen	1·7220	6	1·7241
Oxygen	4·6159	2	4·5979
Water	5·1000	2	5·1724

The salt consequently has the formula

$$N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3 + NH^4O, SO^3 + 2HO.$$

Direct determinations of the amount of the water gave the result—

	I.	II.	III.		
$N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3 + NH^4O, SO^3$	..	..	..	330	94·8276
Water	5·1620	5·1708	5·1788	18	5·1724

and the analysis of the salt dried at 239° F., gave—

	I.	II.	III.
Mercury	60·6024	60·2899	61·0638
Sulphuric acid	25·0000	24·4738	24·7659

Mercury	60·6520	2	60·6060
Sulphuric acid	24·7465	2	24·2424
Nitrogen	..	2	8·4848
Hydrogen	..	6	1·8181
Oxygen	..	2	4·8487

Hence we obtain the formula

$$N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3 + NH^4, SO^3.$$

The mode of formation of this salt is explained by the following equation:—

$$2(NH^4O, SO^3)+2(HgO)=N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3+NH^4O, SO^3+2HO.$$

Products of the Decomposition of Sulphate of Bimercurammonium by means of Water.—By treatment with water or solution of potash, this double salt furnishes a series of basic compounds, which exhibit a great similarity to the so-called compounds of mercuramine. If cold water be poured over the body, it loses its crystalline nature, and becomes converted into a heavy white powder. The filtrate contains much sulphuric acid, but no mercury. Analysis gave—

	I.	II.	III.
Mercury	82·1593	82·1596	82·1309
Sulphuric acid	9·3766	9·3085	9·3251
Nitrogen	3·3962		

The original solution of peroxide of mercury in sulphate of ammonia may also be directly diluted with water, and by this means a precipitate of the same composition is obtained, as shown by analysis:—

	IV.	V.
Mercury	82·1611	82·0824
Sulphuric acid	9·3894	9·3592
Nitrogen	2·2112	

This leads to the following composition:—

	Average of I.—V.		
Mercury	82·1386	7	82·1597
Sulphuric acid	9·3517	2	9·3896
Nitrogen	3·3037	2	3·2863
Hydrogen	0·4656	4	0·4695
Oxygen	4·7404	5	4·6949

and from this we deduce the formula

$$2(N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3)+3HgO.$$

The action of water upon the double sulphate is represented by the following equation:—

$$7(N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3+NH^4O, SO^3)+6HO$$
$$=2\left[2(N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3)+3HgO\right]+10(NH^4O, SO^3).$$

This body is a heavy, white, earthy powder, from which hot water extracts sulphuric acid. When boiled with dilute solution of potash, it also loses sulphuric acid, and at the same time ammonia is evolved. Hot concentrated solution of potash effects a more fundamental decomposition; ammonia is continually evolved, the body becomes quite yellow, and at last pure oxide of mercury remains. If the freshly precipitated compound be treated with sulphate of ammonia, it is dissolved, and the original double salt is

reproduced. In solution of muriate of ammonia it is completely dissolved with evolution of ammonia. Concentrated and dilute muriatic acid, as also dilute sulphuric acid, readily dissolve the salt, but this is not the case with dilute nitric acid and concentrated sulphuric acid. At 239° F. it becomes yellow without losing in weight. When heated in a glass tube it becomes brown, and water, nitrogen, mercury, and sulphurous acid are driven off. The residue is a yellow mass of protosulphate of mercury, which becomes white on cooling, fuses when strongly heated, and is volatilized without residue. This decomposition may be explained by the following formula:—

$$3\left[2\left(N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3\right)+3HgO\right]=3(Hg^2O, SO^3)+NH^3$$
$$+5N+9HO+3Hg.$$

As is shown by the analyses of this body, it is a less basic compound than the ammoniacal turpeth prepared by Fourcroy, Kane, Millon, Ullgren, and Hirzel, which has the formula

$$N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, 2HgO, SO^3.$$

From its behaviour towards hot water, the author supposed that the latter compound also might be prepared from the sulphate of bimercurammonium. He therefore boiled this double salt for a long time with water, poured the fluid away frequently, and continued the boiling with fresh portions of water until the filtrate no longer contained sulphuric acid. By this means he obtained a white powder, becoming yellow when dried, the behaviour of which towards potash, muriate of ammonia, and acids was similar to that of the preceding body, and which also furnished similar products of decomposition at high temperatures, namely, nitrogen, water, mercury, and sulphurous acid. The analysis of the substance dried at 239° F., gave—

		According to Kane.	According to Hirzel.		
Mercury	83·3271	83·43	83·31	4	83·3333
Sulphuric acid	8·3540	8·25	8·67	1	8·3333
Nitrogen	2·9205	..	..	1	2·9166
Hydrogen	0·4158	..	..	2	0·4166
Oxygen	4·9826	..	..	3	5·0002

Hence the body has the formula

$$N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3+2HgO,$$

and is identical with Kane's ammoniacal turpeth. Its formation takes place according to the following equation:—

$$2\left(N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3+NH^4O, SO^3\right)+2HO$$
$$=N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3+2HgO+3(NH^4O, SO^3).$$

The decomposition at a high temperature is explained by the following formula:—

$$N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3+2HgO=Hg^2O, SO^3+2HgO+3(NH^4O, SO^3).$$

Products of the Decomposition of Sulphate of Bimercurammonium by means of Potash.—The double salt is dissolved in so much dilute sulphuric acid that no decomposition occurs. For this purpose the salt must be gradually introduced into the acid, and care must be taken that the latter is always present in excess, as otherwise an insoluble compound separates. The solution in sulphuric acid is poured into an excess of dilute solution of potash, by which a white precipitate is immediately produced with evolution of ammonia. This is washed with warm water until the filtrate is free from sulphuric acid. The body remains as a white, heavy, colouring powder, which becomes yellowish white at 239° F. It dissolves with evolution of ammonia when boiled with solution of muriate of ammonia, and also, but without evolution of ammonia, when boiled with a solution of sulphate of ammonia, by which means the original double compound is reproduced. The salt is readily soluble in dilute and concentrated muriatic acid, and also in very dilute sulphuric acid, but is insoluble in nitric acid and concentrated sulphuric acid. By boiling with dilute solution of potash, ammonia is also evolved, and the white colour becomes yellowish; by longer boiling, complete decomposition is induced and pure peroxide of mercury remains. When heated in a glass tube the body becomes brown, then water is driven off, and afterwards mercury and nitrous acid; a half-fused reddish-brown body remains, which becomes white on cooling, and when more strongly heated is completely volatile, with evolution of sulphurous acid. Analyses of the salt, dried at 239° F., gave—

	I.	II.
Mercury	85·3113	85·1275
Sulphuric acid	6·5903	6·4241

From which we obtain the composition:—

	Average.		
Mercury	85·2194	5	85·0340
Sulphuric acid	6·5072	1	6·8027
Nitrogen	..	1	2·3807
Hydrogen	..	2	0·3401
Oxygen	..	4	5·4425

and consequently the formula

$$N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3+3HgO.$$

Its formation is explained by the following equation:—

$$5(N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3+NH^4O, SO^3)+8KO$$
$$=2(N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3+3HgO)+8NH^3+8KO, SO^3,$$

and its decomposition at a high temperature by

$$3(N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3+3HgO)$$
$$=3(Hg^2O, SO^3)+2NO^3+NH^3+3HO+9Hg,$$

or, as the ammonia could not be ascertained in consequence of the conversion of nitrous acid and ammonia into nitrogen and water,

$$=3(Hg^2O, SO^3)+NO^3+2N+6HO+9Hg.$$

According to the author, this compound, which is produced by the treatment of the original double compound with cold solution of potash, is identical with that formed by boiling ammoniacal turpeth with dilute solution of potash. The author has ascertained by direct experiment, that the latter body also may be completely decomposed by the long action of the reagent.

[To be continued.]

On Solanine. *By* MM. Zwenger *and* Kind.

Solanine is well known to be only a weak base. The authors have found that when it is boiled for a time with dilute sulphuric or muriatic acid, solanine is decomposed into a new strong base and grape-sugar. The new base is called *solanidine* by the authors. No further subsidiary products are formed; so that solanine is a glucoside.

As soon as solanine is boiled with muriatic or sulphuric acid, crystals separate from it, which increase in quantity on cooling. Sometimes also a resinous deposit is formed; but this, when water is poured over it, solidifies in a perfectly crystalline form. This crystalline precipitate contains the acid employed, in combination with solanidine. The salts of this new alkaloid are but sparingly soluble in water and an excess of acid. By recrystallization from absolute alcohol they are easily obtained pure and in well-formed crystals. Their alcoholic solutions, when mixed with ammonia, give a gelatinous precipitate of pure solanidine. This alkaloid is scarcely soluble in water, but dissolves readily in alcohol and æther, and may be obtained crystallized from these solutions. It has a strong alkaline reaction and a bitter taste; it neutralizes acids completely, gives a crystallizable double salt with chloride of platinum, and when carefully heated may be sublimed almost without decomposition in beautiful crystals. When brought in contact with an excess of sulphuric acid and left to stand for a long time, it has the property of giving the fluid an intense red colour,—a property which enables the smallest trace of solanidine to be detected. It had previously been observed that under certain circumstances sulphuric acid possesses the power of giving a red colour to solanine; this phænomenon is not, however, due to solanine as such, but the solanidine formed causes the reaction.

From the mother-liquor of solanidine the authors have obtained crystallized grape-sugar.—Liebig's *Annalen*, cix. p. 245.

On the Constitution of Scammony. By FRANZ KELLER.

The author has previously stated that scammony is a glucoside, and, continuing his investigations upon this body, has found that the products of decomposition which he obtained from the resin were not pure substances; he has now obtained definite products of decomposition in the following ways:—

1. *Decomposition of the Resin by Acids.*—If a solution of the resin, not too dilute, which has been repeatedly purified by animal charcoal, be mixed with an equal volume of English sulphuric acid or supersaturated with muriatic acid gas, the whole of the resin is completely decomposed in the course of about 8 days. If it be then diluted with water, fatty crystalline scales separate; these unite in flakes, rise to the surface, and subsequently contract into a shining crystalline film, the individual crystals of which belong to the clinorhombic system. The flocculent body obtained by the addition of water was collected on a filter, and washed with water. It then usually appears of a dazzling whiteness, and, when dried, forms a scaly laminar mass, like cholesterine. It is fused again in very dilute solution of potash, and then repeatedly in water, by which means a coarsely radiate mass is obtained, which is insoluble in water, but readily soluble in alcohol, on the evaporation of which it shoots into large, brittle, transparent laminar crystals of the above-mentioned system. These have at first scarcely any taste, but gradually produce an unpleasant sensation in the throat. The alcoholic solution has a perfectly neutral reaction. When fused upon water, the crystals flow into an oil of a slightly yellowish colour, which solidifies at 80°—82° F., forming a brittle crystalline mass with a shining surface, which appears composed of large laminæ, especially when slowly cooled. The analysis of this body gave:—

C	73·39	73·57	73·63	28	=168	73·68
H	12·48	12·55	12·42	28	28	12·28
O	14·13	13·88	13·95	4	32	14·04

If this neutral body be dissolved in solution of potash, the potash-salt of an acid produced from it is obtained. This separates, on the addition of sulphuric acid, in white flakes, which unite to form oily drops when heated; on cooling, these appear as beautifully satiny masses. The alcoholic solution has a decidedly acid reaction.

The crystals obtained from the alcoholic solution are less lustrous, and consist of needles grouped like wavellite round a central point, which are also formed by the fused acid on cooling. The melting-point was found to be 140—142° F. The acid produced by potash from the first-mentioned neutral body, and separated by sulphuric acid, was dissolved in alcohol with the addition of an excess of ammonia; and this solution was precipitated by nitrate of silver. The flocculent precipitate obtained gave on analysis

C	49·39	49·26	30	=180	49·58
H	7·89	8·09	27	27	7·43
O	..	..	6	48	13·24
Ag	29·33	29·63	1	108	29·75

The analysis of the free acid gave

C	70·28	70·01	30=180		70·31
H	11·13	12·00	28	28	10·93
O	18·59	17·99	6	48	18·76

Consequently the neutral body has the composition $C^{28}H^{28}O^4$, and would be isomeric with the aldehyde of œnanthylic acid.

The acid produced therefrom by potash would have the formula $C^{30}H^{28}O^6$.

The author now found that in dissolving the neutral body in potash a volatile body escapes, which may be distilled off from the solution and collected in a receiver; this volatile body proved to be an alcohol of the formula $C^{26}H^{28}O^2$. This alcohol is best obtained directly by the treatment of scammony in its alcoholic solution with potash, as follows:—

2. *Decomposition of the Resin by Potash.*—If fragments of hydrate of potash be added to the colourless, boiling, alcoholic solution of the resin, this immediately acquires a yellow colour. When the boiling is continued, the fluid becomes turbid with separation of dark flakes, which only dissolve with difficulty in boiling alcohol, are precipitated again on cooling, and can be completely separated by a further addition of alcohol. The supernatant clear fluid, when mixed with much water, separates an abundance of flakes, which may readily be collected; and this flocculent body is nothing but the volatile alcohol just mentioned.

The remaining alcoholic fluid contains valerianate of potash.

To obtain the above-mentioned alcohol in a pure state, the alcoholic fluid obtained from the decomposition of the resin, which is still rich in potash, is put into a retort, when the alcohol is distilled off and replaced with water. When the last traces of alcohol have passed over, the wall of the retort becomes coated with a thin fatty layer, which gradually passes into the ascending tube, and then into the refrigerating tube, from which it issues in the form of a gelatinous stopper. In order to prepare larger quantities, it is better to employ the resin itself, distilling it in very spacious retorts with solution of potash not too concentrated.

The formation of this body also takes place with baryta-water.

If the masses of the volatile body be fused upon water, they flow into a perfectly clear oleaginous stratum, which, on cooling, exhibits a very delicate crystalline structure. The melting-point in the capillary tube, employing two glasses standing one within the other, was found to be exactly 104° F., which is also the point of solidification. Analysis gave:—

C	77·95	78·06	26=156		78
H	14·08	14·15	28	28	14
O	7·97	7·79	2	16	8

As this volatile alcohol is produced from the neutral body $C^{28}H^{28}O^4$, which the author regards as allied to the aldehydes, the formation of the acid first described and of the alcohol is as follows:—

$$2.(C^{28}H^{28}O^4)=C^{26}H^{28}O^2+C^{30}H^{28}O^6.$$

Liebig's *Annalen*, cix. p. 209.

On the Action of different Æthers upon Sodium-alcohol and upon Ethylocarbonic Acid. *By* Fr. Beilstein.

The experiments of Mr. Williamson have made known that chloride and iodide of ethyle are decomposed in the presence of sodium-alcohol, giving chloride or iodide of sodium and common æther: on substituting organic æthers, such as acetic, for chloride of ethyle, a reaction is manifested, but there is no formation of any ordinary æther.

When acetic æther is added to a solution of sodium-alcohol, there is formed immediately, or in a few moments, a gelatinous white precipitate, usually having a slight yellowish tinge. The liquid will only filter at the outset, and in order to obtain the precipitate dry, it is requisite to press it between folds of filtering-paper. We thus finally obtain a crystalline mass, which presents the composition of acetate of soda. It contains 28·16 per cent. of sodium, acetate of soda contains 28·05 per cent. These experiments, several times repeated, have always yielded the same result; the quantity of sodium varied between 27·85 and 28·17 per cent.

Supposing that a liquid combination had been formed, I analysed the filtered liquid; it presented the composition of a mixture of acetic æther and alcohol.

	Experiment.	Alcohol.	Acetic æther.
G	54·1	52·17	54·55
H	10·6	13·04	9·09

From these facts it appears that in this reaction there is a simple addition of two molecules of acetic æther and sodium-alcohol; and I am the more convinced of this from remarking no evolution of gas, nor any other secondary reaction. The combination formed is very unstable, strongly attracts water, becoming decomposed into alcohol and acetate of soda:—

$$\left.\begin{matrix}C^2H^5\\Na\end{matrix}\right\}O+\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}O+\left\{\begin{matrix}H\\H\end{matrix}\right\}O=\left.\begin{matrix}C^2H^3O\\Na\end{matrix}\right\}O+2C^2H^6O.$$

In the hope of obtaining the compound in a state of purity, I prepared it in a flask closed by a stopper in which were placed two tubes. I drove off the excess of alcohol and acetic æther by heating the flask on the water-bath, and causing a current of dry air to pass over the surface of the liquid. At this temperature the substance fuses, in cooling it becomes solid; the colour was brown. It contained 24·5 per cent. of sodium, while the compound under consideration would only contain 14·74 per cent.

On adding water to the combination, the liquid became heated; by distillation a great quantity of alcohol could be obtained; the residue possessed a strongly marked alkaline reaction.

Repeated with benzoic æther, these experiments gave an analogous result. When benzoic æther is added to a solution of sodium-alcohol, the whole liquid in a few moments becomes a solid mass. Pressed between filtering-paper, it yields on analysis 15·88 to 16·74 per cent. of sodium; the benzoate of soda contains 15·97 per cent.

When oxalic æther is added to a solution of sodium-alcohol, in a few moments there falls a yellow, gelatinous precipitate, probably a combination of the two substances; but not being able to isolate the compound, I have not pursued the study of this reaction.

Lastly, I repeated these experiments with nitric æther. This time no precipitate was formed; but on heating the two substances in a sealed tube on the water-bath, the liquid became brown, and after an hour or two a precipitate was deposited. On opening the tube, the presence of ordinary æther was readily ascertained, and the precipitate was nitrate of soda. It contained 26·75 per cent. of sodium; nitrate of soda contains 27·06 per cent.

We may conclude then from the foregoing that only the inorganic æthers, such as the chloride, iodide, or nitrate of æthyle, are decomposed with sodium-alcohol into ordinary æther and a salt of soda, and that the organic æthers combine with sodium-alcohol, producing very unstable compounds. But these compounds are not decomposed by heat into æther and a salt of soda; I have never observed a trace of æther, probably because, at the temperature at which this decomposition would take place, the combination is already destroyed.

In the hope of obtaining lactic acid, I studied the action of carbonic acid on sodium-alcohol, but only obtained a body isomerous with lactic acid,—ethylocarbonic acid. When a current of dry carbonic acid is brought in contact with a solution of sodium-alcohol, a white precipitate immediately falls, consisting of ethylocarbonate of soda. It contains 20·79 per cent. of sodium; ethylocarbonate of soda contains 20·54 per cent. We have therefore

$$\left.\begin{matrix} C^2H^5 \\ Na \end{matrix}\right\} O + CO^2 \left\{\begin{matrix} CO \\ C^2H^5, Na \end{matrix}\right\} O^2.$$

The ethylocarbonate of potash has been prepared by MM. Dumas and Peligot by the action of carbonic acid upon a solution of potash in absolute alcohol; but the formation of a great quantity of carbonate and bicarbonate of potash renders necessary the rectification of the product. The process which I have just described is recommended for the preparation of the salt of soda, by the facility and rapidity of its execution.—*Comptes Rendus*, May 16, 1859.

On the Decomposition of the Metallic Sulphurets by Chloride of Phosphorus. *By* Dr. R. Weber.

In a former memoir the author has described the action of pentachloride of phosphorus upon the compounds of oxygen, and shown that a great number of simple oxides, such as even silicic acid, calcined alumina, and oxide of chrome, and also the most various salts, for example sulphate of baryta, phosphate of baryta and tungsten, are decomposed at a red heat by the vapour of chloride of phosphorus. In these actions a portion of the chlorine of the chloride of phosphorus is transferred to the radical of the oxide, whilst the corresponding oxygen takes the place of the chlorine.

The products of decomposition consist of the metallic chlorides corresponding with the oxides and oxychloride of phosphorus.

The author has since occupied himself with the action of chloride of phosphorus upon the metallic sulphurets, making use in these experiments of the same apparatus that he formerly employed. The behaviour of a number of native and artificial sulphurets was investigated, and it was found that the decomposition of these took place generally more readily than that of the oxides, and that in this case also it is sometimes attended with incandescence.

Iron pyrites, zinc blende, sulphuret of bismuth, realgar, grey sulphuret of antimony, and galena are very readily and completely decomposed. The latter exhibits the phænomenon of incandescence very beautifully. During the action of chloride of phosphorus upon galena, there is first formed a product of a brownish-red colour, probably a compound of chloride of lead with sulphuret of lead, which by the longer continuance of the action becomes converted into pure chloride of lead. Iron pyrites only furnishes volatile products by its decomposition, the sole residue being a trace of gangue. In the same way the native sulphurets of arsenic and cobalt and ruby blende are readily decomposed; the latter leaves pure chloride of silver. Bournonite, Fahlerz, &c. behave like the other sulphurets. The metallic arseniurets, such as arseniuret of iron and copper-nickel, are acted upon with more difficulty.

In these decompositions metallic chlorides and a fluid product are formed; the latter contains sulphur, chlorine, and phosphorus. It may be readily isolated in the decomposition of galena; it is a yellow oily fluid of a penetrating odour, heavier than water, by which it is very slowly decomposed with separation of sulphur. The solution contains muriatic acid, phosphoric acid, and hyposulphurous acid. Nitric acid decomposes the compound and separates sulphur, which, however, still contains chlorine, a circumstance that adds greatly to the difficulty of the analysis.

From his experiments the author arrives at the conclusion, that this fluid consists principally of a compound analogous in composition to oxychloride of phosphorus. A compound of this nature was first obtained by Serullas by the action of sulphuretted hydrogen upon pentachloride of phosphorus. The separation of the excess of chloride of phosphorus has not yet been successfully effected.

The process taking place in the decomposition of the sulphurets is consequently very similar to that occurring with the oxides. The sulphur combined with the metals is transferred to the phosphorus in the same way as the oxygen of the oxides, whilst the metal combines with a portion of the chlorine of the chloride of phosphorus. The reaction which takes place is readily explicable from the great affinity of sulphur for phosphorus and of chlorine for the metals.

By the direct combination of chloride of phosphorus with sulphuret of phosphorus, the author has also obtained a compound consisting of $PCl^3 S^2$, it therefore has the same constitution as that of Serullas, and by it the above decomposition of the metallic sulphurets receives full confirmation. Thus if corresponding quan-

tities of pentasulphuret of phosphorus, obtained by fusing together sulphur and red phosphorus, and pentachloride of phosphorus be gently heated in a glass tube, and the residue, after the fluid formed has been poured away from the undissolved sulphuret of phosphorus and the crystals deposited, be again heated, it becomes almost entirely converted into an oily fluid, which exhibits all the properties of the compound described by Serullas. Pure chloride of aluminium is not reddened by it, which proves that no sesquichloride of sulphur is present.

If the vapours of pentachloride of phosphorus be conducted over heated sulphur, a fluid is obtained, which strongly reddens chloride of aluminium, and is probably a mixture of sesquichloride of sulphur with the above compound.

By the action of pentachloride of phosphorus upon seleniuret of lead, the author obtained chloride of lead together with a reddish fluid containing selenium, which is decomposed by water with separation of selenium. The solution contains seleniuretted hydrogen, together with other compounds.—*Bericht der Akad. der Wiss. zu Berlin*, 1859, p. 325.

On the Conversion of Acetal into Aldehyde. *By* F. Beilstein.

Wurtz and Frapolli have transformed aldehyde into acetal. The author has effected the opposite transformation of acetal into aldehyde. If acetal be heated for two days to 302°—392° F. with crystallizable acetic acid, acetic æther is obtained as already indicated by Wurtz; but if the product of the reaction be distilled, and the portion passing below 140° F. be received in ammoniacal æther, crystals of aldehyde-ammonia are formed. Aldehyde is formed in these circumstances by the following reaction:—

$$\underbrace{C^6H^{14}O^2}_{\text{Acetal.}} + \underbrace{C^2H^4O^2}_{\text{Acetic acid.}} = \underbrace{C^4H^8O^2}_{\text{Acetic æther.}} + \underbrace{C^2H^4O}_{\text{Aldehyde.}} + 2H^2O.$$

Anhydrous acetic acid reacts similarly upon acetal; when heated with the latter to 302°—392° F. for two days, it furnishes aldehyde and acetic æther. The following is an analysis of this æther:—

	Found.	Calculated.
Carbon	54·3	54·5
Hydrogen	9·9	9·1

If the two substances be heated together in the proportion of 1 equiv. of anhydride, $C^4H^6O^3$, and 1 equiv. of acetal, $C^6H^{14}O^2$, the reaction takes place as just indicated; only a few drops of a liquid boiling above 302° F. are obtained; this probably consists of the combination of anhydrous acetic acid and aldehyde discovered by M. Geuther. However, as in the preceding experiments 1 molecule of aldehyde is always set free in the decomposition of 1 molecule of acetal, it might be expected that, by decomposing acetal by perchloride of phosphorus, the compound $C^4H^4Cl^2$, prepared by Wurtz by treating aldehyde with that reagent, and which he has

called chloride of æthylidene, might be obtained. This, however, has not been realized.

The author's experiments lead him to think that acetal may be referred to a single molecule of water, and that its constitution may be expressed by the formula

$$\left.\begin{matrix} C^4 H^9 O \\ C^2 H^5 \end{matrix}\right\} O,$$

which represents the æthylated compound of an alcohol containing the radical $C^4 H^9 O$. The intermediate compound of MM. Wurtz and Frapolli, $C^4 H^9 O, Cl$, would be the chloride corresponding with this alcohol. It must be remarked, however, that this radical, $C^4 H^9 O$, is not very stable, and that it may be easily split into a molecule of æthyle and a molecule of aldehyde in the reactions to which acetal is subjected.—*Comptes Rendus*, June 20, 1859, p. 1121.

ANALYTICAL CHEMISTRY.

New Process for the separation of Phosphoric Acid from Bases, especially from Alumina and Oxide of Iron. By F. Schulze.

It is well known that the separation of phosphoric acid from alumina and oxide of iron is attended with difficulties. The author has found that it may be separated from acid solutions containing various bases, and especially the two just mentioned, by means of perchloride of antimony, and he recommends the following process in the analysis of arable soils:—

About 50 grms. of soil are calcined in order to destroy the organic matter, and treated with muriatic acid; the phosphoric acid is then to be determined in the solution. The acid fluid is first mixed with very dilute ammonia, and stirred until the free acid is nearly neutralized; this point is recognizable by the reddish colour assumed by the mixture, although no persistent precipitation of oxide of iron may have occurred. This mixture, the volume of which is about 1 litre, is well stirred with a glass rod, then mixed with 35 to 45 drops of perchloride of antimony, and left to stand for 12—24 hours, in which time the formation of the yellowish-white, flocculent precipitate is completed. This, when the operation has been carried on as above described, and especially when the approximate neutralization of the free acid by ammonia has not been neglected, includes the whole of the phosphoric acid present in the solution, but consists principally of hydrated antimonic acid, together with a portion of oxide of iron and alumina unavoidably carried down by the antimonic acid, even when the fluid was strongly acid before the dropping in of the perchloride of antimony. It appears that the presence of the ammoniacal salt in the solution has an influence on the complete precipitation of the phosphoric acid; the precipitate also contains ammonia in proportion to the amount of phosphoric acid, exactly like that which is produced in course of time in the solution of a salt of ammonia, when mixed with an aqueous solution of

antimonic-phosphoric acid. The separation of the phosphoric acid from the precipitate, after it has been washed with distilled water upon a filter, is best effected by boiling with a solution of soda containing a small quantity of silicate of soda. For this purpose it is mixed with a sufficient quantity of the solution of soda, and boiled for a few minutes; after cooling, when it may be assumed that all the antimoniate of soda has separated by crystallization, it is to be filtered. The antimoniate of soda, together with the oxide of iron and the greater part of the alumina, which is combined with silica, remains upon the filter. The alkaline filtrate, which contains the phosphoric acid and a small quantity of alumina containing silica, is supersaturated first with muriatic acid and then with ammonia; it is then evaporated to a small volume, again mixed with ammonia, and filtered. The alumina remaining on the filter retains a small quantity of phosphoric acid, notwithstanding its containing silica; it is dissolved by a drop or two of muriatic acid, the solution evaporated to dryness, and the heated residue treated with water containing muriatic acid; the fluid filtered from the silica is mixed with a little tartaric acid, and then added to the ammoniacal fluid which contains the principal part of the phosphoric acid. Solution of chloride of magnesium containing muriate of ammonia throws down the phosphoric acid from this mixture in its well-known form.—Liebig's *Annalen*, cix. p. 171.

On some Modifications in the Method of analysing Air by Absorption, which facilitate its employment in distant stations. *By* C. Sainte-Claire Deville *and* L. Grandeau.

The principle of construction of the apparatus exhibited by the authors to the Academy of Sciences, is the same as that employed by Brunner, Dumas, and Boussingault. The different elements of the air (with the exception of the nitrogen) are fixed by means of absorbents contained in vessels which are weighed before and after the experiment.

The means of completely retaining the atmospheric water and carbonic acid, consist simply in a sufficient multiplication of the points of contact and a sufficiently slow flow.

In Brunner's experiments the oxygen was absorbed by phosphorus. For this reagent Dumas and Boussingault substituted metallic copper, prepared under certain conditions, and heated to redness in a glass tube in which a vacuum could be produced at pleasure. The authors have employed in the same manner, and concurrently with this reagent, protoxide of manganese, the great oxidizability of which, and especially the comparatively great weight of oxygen which its porosity allows it to absorb, render it valuable in such cases*; it may easily be obtained in abundance in a pure state by reducing the native peroxide or the artificial oxalate by hydrogen.

The carrying on of small quantities of aqueous vapour, probably

* This reagent was employed by M. Sainte-Claire Deville to obtain from air a current of perfectly pure nitrogen.

resulting from the condensation by the finely divided reagent of a portion of the hydrogen used in its reduction, is to be provided against.

The employment of protoxide of manganese in some analyses made in May and June 1859, gave the following numbers: weight of

Oxygen	23·09
Nitrogen	76·91

and in volume (admitting the densities 1·1056 and 0·972 adopted by all physicists)—

Oxygen	20·88
Nitrogen	79·12

The method has the advantage of enabling unlimited portions of air to be operated upon, so as to determine with accuracy the elements which only exist in very small quantities in the atmosphere. In the mode in which it was applied by Dumas and Boussingault, the necessity of weighing a large balloon filled with nitrogen compels the use of an extraordinarily large balance, which it is inconvenient to transport to such places as the tops of mountains. The authors therefore propose to measure the volume of nitrogen instead of weighing it. In their memoir they describe in detail the precautions which they took to ensure accuracy, and from the agreement of their results with those obtained by others, they think that physicists may be induced to try their method in order to its application in distant localities.—*Comptes Rendus*, June 20, 1859, p. 1103.

PROCEEDINGS OF SOCIETIES.

Royal Society.

May 5, 1859. (Sir Benjamin C. Brodie, Bart., Pres., in the Chair.)

"On the Synthesis of Acetic Acid." By J. A. Wanklyn, Esq.

I have elsewhere* shown that a salt of propionic acid results when carbonic acid is brought into contact with a compound consisting of ethyle and an alkali-metal. Guided by a well-known principle, I also inferred that an analogous reaction is common to the whole vinic series.

Believing, however, that it was desirable to investigate other members of the series, I have since undertaken the case of the corresponding methyle-compound, and find that it fully bears out the law, as will be manifest from the following details.

Some sodium-methyle in mixture with zinc-methyle, zinc, sodium, and ether was obtained by acting with sodium upon a strong ethereal solution of zinc-methyle. The product so obtained was divided into two portions—one of which was exposed to the action of a current of dry carbonic acid, and the other reserved for comparison.

During the transmission of carbonic acid, the sodium-methyle became hot. After the completion of the reaction, the resulting

* See Quarterly Journal of the Chemical Society, July 1858, page 130.

solid was treated with a little mercury, in order to convert any free sodium into an amalgam, which would not decompose water with too great violence.

Subsequent distillation of the product, with excess of dilute sulphuric acid, yielded a distillate having most distinctly the smell and taste of acetic acid. This acid distillate was redistilled, when it proved to be free from sulphuric acid.

Some of it was converted into a silver-salt by digestion with oxide of silver. This silver-salt was dissolved in hot water, filtered hot, and allowed to crystallize on cooling. An abundant crop of crystals separated, which was drained from the mother-liquor, the employment of a filter being avoided. The crystals were afterwards dried *in vacuo* over sulphuric acid until they no longer lost weight.

Determinations of silver were made by ignition, the resulting silver being reheated and reweighed until it remained constant.

I. ·0894 gramme of the salt gave ·0580 gramme of metallic silver.

II. ·1597 gramme of the salt gave ·1022 gramme of metallic silver.

Comparison of these results with the composition of acetate of silver gives as follows:—

	Calculated.	Found.	
		I.	II.
Per-centage of Silver.....	64·67	64·88	64·00

which leaves no doubt as to the presence of acetic acid.

Still further proof of the same was obtained by converting a little of the acid into a soda-salt, and heating it with arsenious acid. Abundance of kakodyle was evolved.

In order to remove any doubt which might exist as to the source of this acetic acid, and to show that it did not arise from oxidation of the ether which accompanied the sodium-methyle, I operated upon some of the original sample which had never been exposed to carbonic acid, and which, as previously mentioned, had been laid aside for comparison.

I mixed it with a little mercury, distilled with excess of dilute sulphuric acid, and digested the redistilled distillate with oxide of silver, using the same samples of acid and of oxide of silver as in the former experiment.

The distillate neither smelt like acetic acid, nor yielded acetate of silver on spontaneous evaporation to dryness *in vacuo* of its product with oxide of silver. Neither could kakodyle be obtained on heating its soda-residue with arsenious acid.

From all which, it is evident that the acetic acid obtained must have been the product of the action of carbonic acid. The following conclusion is, therefore, established:—

Dry carbonic acid is decomposed by sodium-methyle with evolution of heat, and production of acetate of soda.

Sodium-methyle. Acetate of soda.

$$C_2O_4 + \overbrace{Na\,C_2H_3} = \overbrace{C_2O_2\,C_2H_3 \atop Na}\Big\}O.$$

I hope also to be able to present shortly an account of the action of carbonic acid on one of the higher compounds of the alkali-metals—most probably on potassium or sodium-amyle.

May 12. (Sir Benjamin C. Brodie, Bart., President, in the Chair.)

"On the Atomic Weight of Graphite." By Benjamin C. Brodie, Esq., F.R.S., Pres. C.S., Professor of Chemistry in the University of Oxford.

In this paper the author arrives at the following results:—That carbon in the form of graphite forms a system of peculiar compounds, different from any compounds of carbon yet known, and capable of being procured only from graphite. That graphite, within certain limits, functions as a distinct element, capable indeed of being converted by certain processes of oxidation into carbonic acid and thus identified with the other forms of carbon, but having a distinct atomic weight, namely 33 (H=1).

After the detail of certain experiments by which the author was led to believe in the existence of a distinct system of compounds of graphite, an account is given of a peculiar crystalline substance formed by the prolonged oxidation of graphite. This substance consists of transparent plates of a pale yellow colour, which exhibit under the microscope an appearance distinctly crystalline. The analysis of this substance gave for its formula $C_{11} H_4 O_5$ (C=12, O=16). From the ratio of the hydrogen to the oxygen in this substance, from the circumstance that it is procured from graphite alone, and from its general physical properties, it is inferred that this substance is the term in the system of graphite which corresponds to the compound of silicon, oxygen and hydrogen, in the system of silicon, procured by Wöhler from the graphitoidal form of that element, and to which Wöhler has assigned the formula $Si_4 H_4 O_5$ (Si=21). If it be assumed that this conclusion is correct, the further inference is that the bodies are similarly constituted. On this hypothesis, to arrive at the atomic weight of graphite, the total weight of carbon, 132, is to be divided by 4, which gives the number 33; and for the formula of the body, putting Gr=33, we have $Gr_4 H_4 O_5$.

This conclusion is confirmed in a remarkable manner by the specific heat of graphite. The specific heat of the elemental bodies varies inversely with their atomic weight. This law is so well established, that Regnault has even proposed to determine the atomic weight by it exclusively. There are, at any rate, only two numbers which can be assigned as the product of the specific heat into the atomic weight of the elemental bodies, namely, approximately the numbers 3·3 and 6·6. But to this law there is one singular exception. Carbon in all its forms is anomalous. The specific heats of diamond, graphite, and wood-charcoal are each different, and taking the atomic weight of carbon as 6 or 12, no one is accordant with the law. The specific heat of graphite is 0·20187. Now,

taking the atomic weight of graphite as 33, we have $33 \times 0{\cdot}201 = 6{\cdot}63$, a result in accordance with the law. The inference is, that the assertion that 33 is the atomic weight of graphite is not only a convenient expression of chemical analysis, but corresponds to a physical fact.

May 19. (Major-General Sabine, R.A., Treas. and V.P., in the Chair.)

"On the Specific Gravity of Alloys." By A. Matthiessen, Ph.D.

Before commencing a research into the electric conductivity of alloys, the author deemed it requisite, as a preliminary step, to determine their specific gravities; and the methods employed and results obtained in this inquiry are given in the present paper.

The metals used were antimony, tin, cadmium, bismuth, silver, lead, mercury, and gold. The silver and gold were obtained in a state of purity from the refiners, the other metals were purified by methods which are described. The quantity prepared of each alloy was twenty grammes. The fused alloys were cast in a form and very thin, to avoid internal cavities from crystallization. Three separate determinations were made of their specific gravity, which, together with the mean result, are given in Tables. In every case the alloy was recast at least three times before the first determination, and once again before each succeeding one. The distilled water used in the weighing was first boiled and allowed to cool *in vacuo*, and the alloys were suspended in it by a fine platinum wire, except the soft amalgams, which were weighed in a tube similarly suspended. In calculating the specific gravities, the weight of water displaced was corrected for the temperature, the unit in all cases being distilled water at 0° C. All the weighings were reduced to a vacuum, and a correction was made for the platinum wire which dipped in the water.

The numerical results are stated in three Tables, of which the first gives the specific gravities of the pure metals employed, and the temperature in Centigrade degrees; the second gives the same of the alloys; and the third exhibits the mean specific gravities found, and the specific gravities as calculated,—1, from the volume of the metals forming the alloy; 2, from their equivalent; and 3, from their weight.

From the last Table it appears that the alloys of antimony are greater in volume than the aggregate of the constituent metals, while those of bismuth, silver, and gold are less. The following alloys expand greatly on cooling, viz. all those of bismuth-antimony, bismuth-gold, and bismuth-silver, which were experimented on; those of bismuth-tin, from Bi_6Sn to Bi_2Sn, the rest of the series very slightly; and bismuth-lead, viz. Bi_6Pb and Bi_4Pb (Bi_2Pb slightly), the rest apparently not at all. Of the bismuth-cadmium series, Bi_6Cd and $BiCd_4$ expand very slightly, the rest not at all. The zinc-alloys are all so very crystalline that no results of value were obtained respecting them.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Oxides of Cerium and the Yellow and Red Sulphates of its Protoperoxide. *By* Professor RAMMELSBERG.

THE yellow and red salts of cerium, which were regarded by Hisinger and Berzelius as persalts, have hitherto been but little investigated. Mosander, indeed, after his discovery of lanthanium and didymium, assumed a protoperoxide of cerium, but others believed they had prepared pure peroxide of cerium; and Hermann especially regarded these coloured salts as compounds of peroxide of cerium, and analysed them, but did not ascertain the degree of oxidation of cerium which forms their base. Marignac was the first to recognize their true nature as double salts of peroxide and protoxide of cerium, but he scarcely investigated their composition. The atomic weight of cerium has been determined by Beringer and Hermann, and lately by Jegel; their results nearly agree in making it 575—576. Marignac stated it at 591, and Kjerulf, in consequence of inaccurate work, at 727. The author's experiments give nearly 576, in close accordance with the first-mentioned number, so that it appears best to regard the number 575 (46 if H=1) as the atomic weight of cerium.

Cerium may be completely freed from lanthanium and didymium, when, in accordance with the process of Hermann, basic sulphate of protoperoxide of cerium is precipitated by water; and all the other compounds may be prepared from this precipitate.

Protoxide of Cerium, CeO, is obtained by heating protocarbonate or protoxalate of cerium in a current of hydrogen gas perfectly free from air. It is a bluish-grey powder, which on exposure to the air is immediately converted into yellowish-white protoperoxide, with a strong evolution of heat. Its hydrate is white, but acquires

a yellow colour by exposure to the air, and becomes converted into a mixture of percarbonate and hydrated protoxide of cerium.

Protoperoxide of Cerium, CeO, Ce^2O^3, is obtained by the ignition of carbonate, oxalate, or nitrate of protoxide of cerium. It is yellowish white, with a slight reddish tinge, acquires a transient yellow colour when heated, and dissolves to form a yellowish-red fluid only in rather concentrated sulphuric acid. In hydrogen gas it is reduced to protoxide, but cannot be more highly oxidized either by heating in oxygen or by fusion with chlorate of potash or hydrate of potash. Its hydrate, which contains 3 atoms of water, is produced by passing chlorine into a solution of hydrate of potash in which hydrated protoxide of cerium is suspended.

From the yellowish-red solution of protoperoxide of cerium in sulphuric acid two salts are obtained:—

A. A brownish-red or yellowish-red salt in hexagonal crystals ($a:c=0{\cdot}4231:1$), the formula of which is $3(CeO, SO^3)+Ce^2O^3$, $3SO^3+18HO$. It is decomposed in water with deposition of a sulphur-yellow basic salt, gives a reddish-grey precipitate, $3CeO+Ce^2O^3$, with hydrate of potash, which acquires a yellow colour and becomes converted into CeO, Ce^2O^3 when exposed to the air, but also attracts a little carbonic acid.

B. A yellow indistinctly crystalline salt, which only contains one-third of the quantity of protosulphate of cerium, $(CeO, SO^3+Ce^2O^3, 3SO^3)+8HO$, and behaves towards water in the same manner as A.

Basic Sulphate of Protoperoxide of Cerium is produced from both the above compounds by decomposition in water. It is a pale yellow precipitate (discovered by Mosander, employed by Hermann in the preparation of pure salts of cerium, and investigated by him and Marignac). It consists of 2 atoms of protoperoxide of cerium, 3 atoms of sulphuric acid, and 6 atoms of water, which may be expressed by $2CeO, SO^3+(2Ce^2O^3, SO^3)+6HO$, or, less appropriately, by $(2Ce^2O, SO^3)+2(Ce^2O^3, SO^3)+6HO$.

When exposed to a strong red heat, these three salts leave pure protoperoxide of cerium.

If a solution of protopersulphate of cerium be mixed with one of sulphate of potash, a yellow crystalline precipitate is obtained. But according to the quantity of the salts, the temperature and degree of concentration, precipitates are produced from which 36—27 per cent. of protoperoxide of cerium and 17—24 per cent. of potash are obtained. These are evidently often mixtures of at least two compounds. From the author's analyses we may conclude that the precipitate containing least potash and most cerium, has 3 atoms of sulphate of potash, and 6 atoms of water to 1 atom of the salt of cerium; and that the precipitates with the largest quantity of potash, consist of a similar compound with double the amount, that is 6 atoms, of sulphate of potash, although the latter was only obtained mixed with the former. At the same time it appears to the author that it would be better to regard these salts as isomorphic mixtures of two double salts;—that is to say, the compound with 3 atoms of sulphate of potash,

$$3(KO, SO^3)+3(CeO, SO^3)+Ce^2O^3, 3SO^3+6HO,$$

as

$$\left(6\begin{matrix}\frac{1}{2}KO\\ \frac{1}{2}CeO\end{matrix}\right\} SO^3+Ce^2O^3, 3SO^3+6HO,$$

and the other,

$$6(KO, SO^3)+3(CeO, SO^3)+Ce^2O^3, 3SO^3+6HO,$$

as

$$\left(9\begin{matrix}\frac{2}{3}KO\\ \frac{1}{3}CeO\end{matrix}\right\} SO^3+Ce^2O^3, 3SO^3+6HO.$$

Sulphate of Protoperoxide of Cerium and Ammonia is produced in the same way. But together with the crystalline-granular precipitate, the composition of which agrees with the formula

$$4(NH^4O, SO^3)+2(CeO, SO^3)+Ce^2O^3, 3SO^3+4HO,$$

or

$$\left(6\begin{matrix}\frac{2}{3}NH^4O\\ \frac{1}{3}CeO\end{matrix}\right\} SO^3+Ce^2O^3, 3SO^3+4HO,$$

very beautiful, large, orange-red crystals are formed, which, according to the measurements of Schabus and Rammelsberg, are triclinometric ($a : b : c = 0{\cdot}8144 : 1 : 0{\cdot}6877$; angle of the oblique axes $= 83° 29'$). They are very perfectly cleavable and trichromatic. They dissolve readily in water. Their composition is

$$9(NH^4O, SO^3)+(CeO, SO^3+2Ce^2O^3+3SO^3)+12HO,$$

or, perhaps better,

$$\left(5\begin{matrix}\frac{9}{10}NH^4O\\ \frac{1}{10}CeO\end{matrix}\right\} SO^3+Ce^2O^3, 3SO^3+6HO.$$

When calcined, they give pure protoperoxide of cerium.

A series of analyses made by the author has given as the formula of cerite,

$$\left.\begin{matrix}CeO, LaO, DiO\\ CaO\\ FeO\end{matrix}\right\}^2 SiO^2+HO.$$

When it is decomposed by muriatic acid, the silicic acid still contains a great quantity of those bases, and what is worthy of notice, the oxides of lanthanium and didymium are in much greater proportion to the protoxide of cerium than in the muriatic solution. —*Bericht der Akad. der Wiss. zu Berlin*, 1859, p. 359.

Researches on Acetone. *By* A. Riche.

I. When a weak electrical current, produced by three Bunsen's elements, is passed into a mixture of acetone and muriatic acid, an abundant evolution of hydrogen takes place at the negative pole, whilst only small quantities of gas are produced at the positive pole. Under the influence of the current, the muriatic acid is decomposed and the nascent chlorine reacts upon the acetone with such energy, that no trace of it is set free, and the liquid is strongly heated.

The liquid, which is at first limpid, soon becomes turbid in consequence of the formation of oily drops which collect at the bottom of the vessel. At the end of eighteen or twenty-four hours the formation of these ceases; the oil is then washed and dried. When distilled, it begins to boil at 194° F., but the greater part passes at 239°—246° F. This portion, agitated with yellow oxide of lead and again distilled, boils at 242°·6 F.; it presents exactly the composition of monochlorinated acetone, and its formula,

$$\begin{matrix} C^6\,H^5\,O^2 \\ Cl \end{matrix}$$

corresponds with 4 volumes of vapour.

It is a colourless and very limpid liquid, which strongly affects the nostrils and irritates the eyes to such an extent as to cause an abundant flow of tears. Its density is 1·14 at 57° F. Its density of vapour is 3·40. This body undergoes no alteration either by contact with the air or by distillation; it does not react upon litmus-paper. It does not mix with water, although it appears to dissolve a little therein with time and when agitated; the liquid obtained is not precipitated by nitrate of silver.

All the experiments made with the view of ascertaining the mode in which the elements are grouped in this body, which has the composition of chloride of propionyle, were fruitless. It was kept for fifty hours in contact with a large quantity of boiling water; it disappeared entirely, and the liquid was precipitated by nitrate of silver; but on evaporating the water, nearly the whole of the body was deposited unaltered.

Aqueous and alcoholic solutions of potash gave brown products; gaseous ammonia, ammonia dissolved in water or alcohol, and solution of carbonate of ammonia act in the same way, giving rise to a deposit of muriate of ammonia.

Recently precipitated oxide of silver attacks it a little in the cold, but the reaction is not completed without difficulty even at 212° F.; a brown liquid is obtained, which is soluble in æther, and becomes gelatinous by evaporation; it did not furnish either acetate or propionate of silver.

II. Solution of hydrobromic acid behaves similarly towards acetone; an oil is deposited in the course of a few hours. This, when washed, dried, and distilled, begins to boil at about 212° F., but the temperature rises rapidly to 284° F. Between 284° and 293° F. a great quantity of the product passes; but during distillation the liquid becomes black in the retort, and evolves hydrobromic acid.

This portion, freed from hydrobromic acid by a current of dry hydrogen and by agitation with yellow oxide of lead, presents the composition of monobrominated acetone,

$$\begin{matrix} C^6\,H^5\,O^2 \\ Br \end{matrix}$$

This body is a colourless liquid, but it becomes brown in a few moments, which has prevented its properties from being studied.

It irritates the eyes so strongly that it is impossible to remain in a place where a few drops of it have been spilt; its transfer from vessel to vessel, its washing, and its distillation, are rendered by this property extremely painful operations.

III. Acetone is acted upon under the same conditions by hydriodic acid; iodine dissolves in the acetone to which it gives a black tint, and an oil much charged with iodine is deposited at the bottom of the vessel. The author did not succeed in driving off the excess of iodine, but after numerous washings he isolated a few colourless needles containing iodine and organic matter; they were in too small quantity for analysis. The iodized compound produced appears to be analogous to the preceding brominated and chlorinated bodies, for the liquid acts strongly upon the eyes and nostrils.

IV. If the current produced by three Bunsen's elements be passed for four or five days through a mixture of two parts of acetone, one part of water, and one part of ordinary nitric acid, the liquid remains limpid, but acquires a strong odour of vinegar. If it be saturated with carbonate of potash, and the salt obtained treated with alcohol, acetate of potash is obtained from it.

The crude salt obtained after the saturation of the acid, evolves alkaline vapours when heated with potash; these consist of ammonia and methylamine. The presence of ammonia is perfectly natural, as an electrical current passed through a solution of nitric acid furnishes much ammonia by the combination of the nascent nitrogen and hydrogen. To explain the presence of methylamine, it must be assumed that the radical methyle, $C^2 H^3$, exists in acetone, or that it is produced concurrently with acetic acid by decomposition.

This experiment would then be the verification of the hypothesis put forth by Gerhardt, who regarded acetone as methyluret of acetyle,

$$C^2 H^3$$
$$C^4 H^3 O^2,$$

aldehyde being the hydruret of acetyle,

$$H$$
$$C^4 H^3 O^2.$$

Besides ammonia, methylamine, and acetic acid, this reaction furnished a small quantity of a substance insoluble in water, which proved to be oxamide; this appears to be a secondary product, as it only occurred twice in three experiments.—*Comptes Rendus*, July 25, 1859, p. 176.

On Dioxymethylene. *By* A. Boutlerow.

An intimate mixture of equal equivalents of oxalate of silver and iodide of methylene, $C^2 H^2 I^2$, when gently heated, reacts energetically and almost with explosion, evolving brown vapours. The reaction may be moderated by adding pounded glass to the mixture, or still better by placing it under a stratum of rectified

naphtha. At a gentle heat, a slow and regular decomposition is manifested. Gases are evolved in abundance, and a new solid and volatile compound is formed. The latter is sublimed, or, carried over by the vapours of naphtha, condenses in the cold receiver, forming a thin, white coat, adhering strongly to the walls of the vessel. Towards the end of the operation oxalic acid sublimes. The gas evolved is a mixture of carbonic acid and oxide of carbon.

The solid, volatile compound is called *dioxymethylene* by the author. Its composition is $C^4 H^4 O^4$, which is confirmed by its density of vapour. It is isomeric with acetic acid. It contains double the elements of the oxide of methylene, $C^2 H^2 O^2$, corresponding to the iodide, $C^2 H^2 I^2$. It might be regarded as the æther of methyloglycol, had not the researches of Wurtz shown that the æthers of the bibasic alcohols contain the same number of equivalents of carbon as the bibasic alcohols themselves. On the other hand, it is possible that the first term of the series may be an exception in this respect.

In any case, dioxymethylene originates by the following reaction:—

$$\underbrace{2\begin{pmatrix} C^4 O^4 \\ Ag^2 \end{pmatrix} O^4}_{\text{Oxalate of silver.}} + \underbrace{2 C^2 H^2 I^2}_{\text{Iodide of methylene.}} = C^4 H^4 O^4 + 4 AgI + 2 C^2 O^4 + 2 C^2 O^2.$$

In this reaction, in which oxalic methyloglycol (oxalate of oxide of methylene) should be formed, the elements of the oxalic acid merely separate from the oxide of methylene, and the latter doubles its molecule. The oxalate of silver behaves here as oxide of silver itself would do; this is proved by the formation of a certain quantity of dioxide of methylene by the reaction, under the naphtha, of oxide of silver upon iodide of methylene.

Dioxymethylene only possesses a faint odour at the ordinary temperature, but when heated it evolves a very strong, irritating and characteristic odour. It has no taste, and is neutral to test-papers. It may be sublimed without fusion. It is volatilized below 212° F., but the evaporation takes place slowly, and only becomes very active above 302° F. At about 306° F. the substance fuses and begins to boil.

Dioxymethylene does not dissolve readily either in water, alcohol, or æther, even at the temperature of ebullition. When heated to 212° F. with water for several hours it dissolves entirely. The solution evaporated *in vacuo* leaves a solid white residue, which appears to consist in great part of the unaltered substance.

With red iodide of phosphorus, dioxymethylene regenerates iodide of methylene. It reduces the oxides of silver and mercury; nitric acid and a mixture of bichromate of potash and sulphuric acid convert it into carbonic acid and water. It is acted upon by gaseous ammonia with formation of a volatile substance which sublimes in crystals, and apparently possesses alkaline properties.—*Comptes Rendus*, July 18, 1859, p. 137.

Further Researches upon Lactic Acid. *By* A. Wurtz.

Having obtained propyloglycol from lactic acid by slow oxidation, the author supposed that the same relations existed between these two bodies as between acetic acid and alcohol, and that lactic acid was to be regarded as a bibasic acid of the formula

$$\left\{\begin{matrix}\bar{C}^3\,H^4\,\bar{O}\\ H^2\end{matrix}\right\}\bar{O}^2\,*.$$

The following facts support this view. The author has succeeded in forming bibasic lactic æther, $\left\{\begin{matrix}\bar{C}^3\,H^4\,\bar{O}\\ (C^2\,H^5)\end{matrix}\right\}\bar{O}^2$, in which 2 equivs. of hydrogen of lactic acid are replaced by 2 equivs. of æthyle.

Lactic Æther.—To prepare this æther, chlorolactic æther is set in action upon æthylate of soda; the chlorolactic æther was obtained by treating chloride of lactyle with alcohol; its identity with chloropropionic æther has just been demonstrated by Ulrich. The reaction is effected as follows:—

$$\underbrace{\left\{\begin{matrix}\bar{C}^3\,H^4\,\bar{O}\\ C^2\,H^5\\ Cl\end{matrix}\right\}\bar{O}}_{\text{Chlorolactic æther.}}+\left\{\begin{matrix}C^2\,H^5\\ Na\end{matrix}\right\}\bar{O}=\underbrace{\left\{\begin{matrix}\bar{C}^3\,H^4\,\bar{O}\\ (C^2\,H^5)^2\end{matrix}\right\}\bar{O}^2}_{\text{Lactic æther.}}+ClNa.$$

It indicates the intimate relations which exist between chlorolactic æther and lactic æther, and consequently lactic acid itself.

In a state of purity lactic æther is a transparent and mobile liquid, possessing an agreeable odour; it boils at 313°·7 F. under a pressure of 0·757 metre. Its density at 32° F. is 0·9203. Its density of vapour was found by experiment to be =5·052. Its calculated density of vapour would be =5·054 for a condensation to 2 volumes†.

Its analysis gave—

	Found.			Calculated.	
	I.	II.	III.		
Carbon	57·86	57·17	57·17	$\bar{C}^7$	57·53
Hydrogen ..	9·67	9·60	9·85	H^{14}	9·59
Oxygen....	..	..	..	$\bar{O}^3$	32·88

These numbers agree with the formula

$$\bar{C}^7\,H^{14}\bar{O}^3=\left\{\begin{matrix}\bar{C}^3\,H^4\,\bar{O}\\ (C^2\,H^5)^2\end{matrix}\right\}\bar{O}^2,$$

which is also confirmed by the density of vapour. Lactic æther is insoluble in water, on the surface of which it forms an oily stratum.

* $\bar{C}=12$; $H=1$; $\bar{O}=16$. The symbols $\bar{C}$ and $\bar{O}$ for carbon and oxygen are barred (1) to indicate the polyatomic nature of these elements, and (2) to facilitate the passage of this notation to the old notation; to effect this it suffices to multiply by 2 the coefficients of the barred letters.

† $H^2\bar{O}=18=2$ volumes.

When an alcoholic solution of lactic æther is saturated with ammonia, and the fluid is heated on the water-bath for several days, the ammonia reacts upon the elements of the æther, and an amide is formed. This body crystallizes in fine, brilliant, fusible laminæ, which are soluble in water and in alcohol. From analysis these crystals consist of lactamethane or lactamic æther,

$$C^5 H^{11} NO^2 = \left\{ \begin{matrix} [C^3 H^4 O]'' H^2 N \\ C^2 H^5 \end{matrix} \right\} O,$$

which is to lactic acid, $\left\{ \begin{matrix} C^3 H^4 O \\ H^2 \end{matrix} \right\} O^2$, what oxamethane or oxamic æther, $\left\{ \begin{matrix} [C^2 O^2]'' H^2 N \\ C^2 H^5 \end{matrix} \right\} O$ (Balard), is to oxalic acid, $\left\{ \begin{matrix} C^2 O^2 \\ H^2 \end{matrix} \right\} O^2$.

We are acquainted with lactates of the form $\left\{ \begin{matrix} C^3 H^4 O \\ M^2 \end{matrix} \right\} O^2$, in which 2 atoms of hydrogen are replaced by 2 atoms of metal. But it must be confessed that the second atom of basic hydrogen in lactic acid is not exchanged without difficulty for an atom of metal, which is also the case with the bibasic salicylic acid. This second atom of basic hydrogen may easily be exchanged for an acid radical. By the reaction of chlorolactic æther upon an alcoholic solution of butyrate of potash, the author obtained an ætherial compound which he regards as the æther of lactobutyric acid, $\left\{ \begin{matrix} [C^3 H^4 O]'' \\ [C^3 H^7 O]' \\ H \end{matrix} \right\} O^2$, derived from lactic acid by the substitution of an atom of butyryle for an atom of hydrogen. Lactobutyric æther is formed by the following reaction:—

$$\underbrace{\left\{ \begin{matrix} [C^3 H^4 O]'' \\ [C^2 H^5]' \end{matrix} \right\} O}_{\text{Chlorolactic æther.}} + \underbrace{\left\{ \begin{matrix} [C^4 H^7 O]'' \\ K \end{matrix} \right\} O}_{\text{Butyrate of potash.}} = ClK + \underbrace{\left\{ \begin{matrix} [C^3 H^4 O]'' \\ [C^4 H^7 O]' \\ [C^2 H^5]' \end{matrix} \right\} O^2}_{\text{Lactobutyric æther.}}$$

This æther forms an oleaginous liquid, which is insoluble in water, soluble in alcohol, possessing an odour resembling that of butyric acid and a density of 1·024 at 32° F. It boils at 406°·4 F. Its density of vapour was found =6·731. Its theoretical vapour-density would be =6·509 for a condensation to 2 volumes.

Its analysis gave—

	Found.				Calculated.
	I.	II.	III.		
Carbon	56·89	57·93	57·01	C	57·44
Hydrogen	8·52	8·41	8·76	H	8·51
Oxygen	..	..	..	O	34·05

The author regards lactobutyric acid as analogous to the benzoglycolic and benzolactic acids of MM. Strecker and Socoloff.—*Comptes Rendus*, June 13, 1859, p. 1092.

On the Mercurial Bases. *By* Dr. Otto Schmieder.

[Concluded from page 308.]

Basic Compounds of Protochloride of Bimercurammonium.—If the double sulphate be dissolved by boiling in muriatic acid, and this solution be treated in the cold with an excess of dilute solution of potash, a white precipitate is produced with evolution of ammonia. The same body is formed (as shown by the following analyses) when the basic sulphate with 3 atoms of oxide of mercury thrown down by potash, is dissolved by boiling in muriatic acid, diluted with water, and mixed at the ordinary temperature with an excess of solution of potash. This white, heavy, earthy body, when dried at 239° F., becomes yellow without losing in weight, dissolves in dilute muriatic acid, with more difficulty in dilute sulphuric and nitric acids, but not in concentrated sulphuric acid. When boiled with a solution of sulphate or muriate of ammonia, it is dissolved with evolution of ammonia. Dilute solution of potash has little action upon it; concentrated solution of potash at length causes total decomposition. Sulphuretted hydrogen decomposes the body into sulphuret of mercury and muriate of ammonia. When heated in a glass tube it gradually becomes brown, then water is evolved, subsequently protochloride of mercury sublimes, and a speculum of mercury is produced.

For analysis the substance was suspended in water, and sulphuretted hydrogen was passed through it. The filtrate from the sulphuret of mercury was mixed with some sulphate of iron in order to destroy the sulphuretted hydrogen, and after standing for 24 hours, the sulphur was separated by filtration. In this filtrate the chlorine was determined by means of silver, and the nitrogen, in another portion, by evaporating the solution of muriate of ammonia. The results I. and II. relate to the original double compound, III. and IV. to the body prepared from the basic sulphate.

	I.	II.	III.	IV.
Mercury	86·8547	86·9491	86·2430	86·6007
Chlorine	6·4035	6·6101	7·4664	6·6453
Nitrogen	2·5313	..	2·5419	

Hence we obtain the centesimal composition:—

Mercury	86·6618	5	86·8809
Chlorine	6·5314	1	6·1685
Nitrogen	2·5366	1	2·4326
Hydrogen	0·3569	2	0·3475
Oxygen	3·9133	3	4·1705

The body consequently has the formula

$$N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.Cl, 3\,HgO;$$

its formation is explained from the great affinity of mercury for chlorine. The sulphuric acid is expelled by chlorine from the sulphate of bimercurammonium with formation of water, sulphuric acid, and

protochloride of bimercurammonium (white precipitate), which is still held in solution by the sulphate of ammonia.

$$(N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3 + NH^4O, SO^3 + ClH$$
$$= N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.Cl + NH^4, SO^3 + HO + SO^3.$$

The decomposition of this solution by potash is explained by the following equation:—

$$5(N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right. + NH^4O, SO^3) + 8KO$$
$$= 2(N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.Cl + 3HgO) + 8NH^3 + 3ClK + 5(KO, SO^3) + 2HO.$$

The formation from the basic sulphate may be explained more simply:—

$$(N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3 + 3HgO) + ClH + KO$$
$$= (N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.Cl + 3HgO) + HO + KO, SO^3.$$

The decomposition at a high temperature takes place as follows:—

$$3(N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.Cl + 3HgO)$$
$$= 3Hg^2Cl + NH^3 + 2NO^3 + 3HO + 9Hg$$
or $$= 3Hg\ Cl + 2N\ +\ NO^3 + 6HO + 9Hg.$$

When this basic salt is boiled with muriate of ammonia it dissolves, ammonia is evolved, perchloride of mercury is formed, and a compound of protochloride of bimercurammonium with muriate of ammonia is produced, exactly analogous to the salt first described. The author is still occupied with the purification of this salt, and therefore gives no analyses; he thinks, however, that he may conclude from his experiments that this compound really exists. In the action of the previously described basic protochloride of bimercurammonium upon muriate of ammonia, the 3 atoms of peroxide of mercury contained in the former exert a decomposing action upon the muriate of ammonia, ammonia being evolved whilst its chlorine passes to the mercury, and another portion of muriate of ammonia combines directly with the protochloride of bimercurammonium which remains undecomposed.

Even from the latter body (white precipitate) the above-mentioned double compound may be obtained when it is dissolved in muriate of ammonia; no ammonia and no bichloride of mercury are formed; the pure double compound crystallizes from the saturated solution.

From white precipitate therefore two basic chlorides may be prepared, of which one contains three, the other two atoms of peroxide of mercury; these compounds are formed according as the precipitate is treated with potash directly or in solution in ammoniacal

salts. They are exactly analogous to the above-described basic sulphates of bimercurammonium, and are produced in a similar manner.

But besides these two basic chlorides, there also no doubt exist several others, which may be prepared from white precipitate. This is attacked by potash as long as it still contains nitrogen. This opinion, which is not in accordance with the prevailing one relating to these bodies (Kane and others assuming that the expulsion of the ammonia is never complete), is supported by the author by the following experiment.

The original double sulphate is dissolved in muriatic acid, and the basic chloride with 3 atoms of oxide of mercury is prepared by means of potash. The precipitate is boiled with fresh potash until the compound, which is at first white, has acquired a yellow colour. The body thus produced possesses the same properties as the basic compound previously described, and furnishes the same products of decomposition at a high temperature, namely protochloride of mercury, water, mercury, nitrogen, and nitrous acid. Its analysis gave :—

Mercury	87·8060	6	87·7834
Chlorine	5·1746	1	5·2084
Nitrogen	.	1	2·0482
Hydrogen	..	2	0·2926
Oxygen	..	4	4·6814

The decomposition at a high temperature takes place in accordance with the following equation :—

$$6(N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.Cl, 4HgO)$$
$$=6(Hg^2Cl)+NH^3+5NO^3+9HO+24Hg$$
or $$=6(Hg^2Cl)+2N+4NO^3+12HO+24Hg.$$

By continued boiling for days with fresh portions of potash, the whole of the chlorine and nitrogen were at last removed from the compound, and pure oxide of mercury was left.

According to these investigations therefore the following salts exist, containing either oxide or protochloride of bimercurammonium :—

1. $N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3+NH^4O, SO^3+2HO.$
2. $N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3+2HgO$ (Kane's ammoniacal turpeth).
3. $2(N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3)+3HgO.$
4. $N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, SO^3+3HgO.$
5. $N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, NO^5+HO$ (Mitscherlich).

6. $N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, NO^5+2HgO$ (Soubeiran).

7. $N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, PO^5+4HgO$ (Hirzel).

8. $N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, CO^2+2HgO$ (Millon).

9. $N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.Cl, NH^4Cl.$

10. $N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.Cl+3HgO.$

11. $N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.Cl+4HgO.$

12. $N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.Cl.$

13. $N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.Cl+2HgO.$

From the results contained in this memoir, the author expresses the following opinion upon the theoretical views mentioned in the introduction:—

Hofmann's investigations upon the ammonias have proved that the hydrogen of ammonium or oxide of ammonium may be replaced by mercury; he called the new base produced either mercurammonium or bimercurammonium, &c., according to the number of atoms of hydrogen displaced. Corresponding with these ammoniaco-mercurial bases, mercuramine and its so-called salts were recognized as containing an oxide of ammonia base in combination with 2 atoms of oxide of mercury, which, according to Millon, as has already been mentioned in the introduction, possesses the properties of a strong base, consisting principally in the fact that oxide of mercury and ammonia, or mercuramine, attracts carbonic acid from the air, sets ammonia free from ammoniacal salts, and may be precipitated from its salts by potash without acid.

Those compounds, which were regarded as salts of this mercuramine, have certainly, accidentally, an analogous composition with the so-called mercuramine; however, from the more careful study of the properties of these compounds, it appears at once that we are not justified in regarding them as salts of mercuramine. For, from these so-called salts of mercuramine, which were obtained exactly in the same way as the above-described compounds, and also possess the same or a similar composition, the complex base (mercuramine) cannot, as Millon states, be precipitated without acids, while, as has been shown in this memoir, the corresponding salt is always again obtained by potash from the solutions of these basic salts.

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All these basic compounds also possess the property, when boiled [illegible] of ammonia, of becoming decomposed with evolution

of ammonia, whilst, on the other hand, sulphate of ammonia dissolves these salts without setting free ammonia.

From the above properties of these compounds it is perfectly clear that they cannot be salts of mercuramine, but that they are nothing but basic products of decomposition of a neutral compound.

As regards the true compound of oxide of mercury and ammonia (mercuramine), it must remain for later investigations to determine its intimate nature, as, from its property of attracting carbonic acid from the air, it appears to possess the character of a strong base.

But hitherto only the compound with carbonic acid has been prepared directly from it, and this exhibits a composition exactly analogous to that of the basic salts just mentioned, and consequently might also be regarded as a basic salt. It is therefore possible, that the property of the compound of oxide of mercury and ammonia (mercuramine), of attracting carbonic acid from the air, only depends on the great affinity of oxide of mercury for carbonate of ammonia, oxide of mercury being dissolved by carbonate of ammonia with the greatest avidity. It may also be assumed with some certainty, that if oxide of mercury were allowed to act upon carbonate of ammonia in the same way and with the same precautions that were employed in the preparation of the double compound of sulphate of bimercurammonium with sulphate of ammonia, an analogous double compound would be obtained, as in this case, as with sulphate of ammonia, no evolution of ammonia takes place. Just as the above-described basic salts are the products of decomposition of a neutral double compound, so would also the other basic mercurammoniacal salts, which are known under the name of mercuramine compounds, be capable of conversion into similar double compounds by treatment with the corresponding ammoniacal salts; but the supposition that these basic salts have the property of entering into double combinations with ammoniacal salts, without at the same time losing the mercuramine type, must be regarded as erroneous; for, indeed, as appears from this memoir, the whole of these basic compounds exert a decomposing action upon ammoniacal salts, partly with and partly without evolution of ammonia. The crystallized compound prepared by Mitscherlich, which he regards as a double compound of nitrate of mercuramine with nitrate of ammonia, in accordance with the formula

$$N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, 2HgO, NO^5 + NH^4O, NO^5,$$

is consequently nothing but nitrate of bimercurammonium with water, as is shown by the following formula:—

$$N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, 2HgO, NO^5 + NH^4O, NO^5$$
$$= 2\left(N\left\{\begin{matrix}H^2\\Hg^2\end{matrix}\right.O, NO^5 + HO\right).$$

The property of the basic mercurammoniacal compounds of forming compounds with the ammoniacal salts, either with or without evolution of ammonia, proves that in this case a decomposition of

a peculiar nature takes place, which finds a simple explanation in the present memoir.

For when muriate of ammonia, for example, is set in action upon these basic compounds (so-called mercuramine salts), bichloride of mercury is formed, whilst at the same time ammonia must be set free from the muriate of ammonia; but here this is not capable, as indeed has been shown by the experiments, of precipitating a mercurial salt from the solution; whilst when sulphate of ammonia is employed, the double compound described in this memoir must be formed.

It follows therefore as the principal result of this memoir, that the mercuramine salts are products of decomposition of a neutral mercurial compound.

A compound of this nature is to be found in the double sulphate of bimercurammonium and ammonia, in which oxide of bimercurammonium forms the base, which has the property of forming compounds with metallic oxides, acids, and salts.

It cannot be denied that this view is the simplest and least forced; it may also be assumed, with great probability, that the so-called mercuramine is not to be regarded as an independent base, but that it is perhaps nothing but oxide of bimercurammonium in combination with oxide of mercury, and the so-called salts of mercuramine are basic compounds of bimercurammonium or its oxide.

The supposition that mercuramine and the mercuramine compounds belong to oxide of tetramercurammonium may be easily shown to be impossible by the formula itself. For as all these salts have the property of evolving ammonia when brought in contact with muriate of ammonia, the decomposition cannot be explained in this way, as is shown by the following formula:—

$$NHg^4O, 2HO, SO^3 + NH^4Cl = NHg^4ClHO + NH^4O, SO^3.$$

A glance at this formula shows distinctly that no evolution of ammonia is possible in this case.—*Journal für Prakt. Chem.*, lxxv. p. 129.

PROCEEDINGS OF SOCIETIES.

Royal Society.

On the Action of Acids on Glycol. By Dr. Maxwell Simpson.

[Received June 29, 1859.]

Since my last communication to the Society*, I have discovered a more convenient process for the preparation of chloracetine of glycol. I have ascertained that the monoacetate of glycol is as readily converted into this substance by the action of hydrochloric acid, as a mixture of acetic acid and glycol. As the monoacetate is easily obtained, and for this purpose need not be quite pure, it is possible by this method to prepare the body in question on a large scale and with great facility. It is simply necessary to conduct a stream of dry hydrochloric acid gas into the monoacetate, maintained at the temperature of 100° C., till the quantity of oil precipitated on the

* Chem. Gaz. Aug. 1, 1859, p. 298.

addition of water ceases to increase. The whole is then well washed with water, dried by means of chloride of calcium, and distilled. Almost the entire quantity passes over between 144° and 146° C. A portion of liquid prepared in this manner gave the following numbers on analysis, which leave no doubt as to its identity :—

	Theory.	Experiment.
C_8....	39·18	39·01
H_7....	5·71	5·83
O_4....	26·14	..
Cl....	28·97	..
	100·00	

The reaction which gives birth to this body may be thus explained :—

$$\left.\begin{matrix} C_4H_4 \\ C_4H_3O_2 \\ H \end{matrix}\right\} O_4 + HCl = \left.\begin{matrix} C_4H_4 \\ C_4H_3O_2 \\ Cl \end{matrix}\right\} O_2 + 2HO.$$

I have made a determination of the vapour-density of chloracetine, and obtained results confirmatory of the formula I have given for this body : experimental vapour-density 4·369, calculated 4·231 for 4 volumes. I have also ascertained that oxide of ethylene is formed, and not glycol, when this substance is acted upon by a solution of potash. The following equation will explain the reaction :—

$$\left.\begin{matrix} C_4H_4 \\ C_4H_3O_2 \\ Cl \end{matrix}\right\} O_2 + 2\left.\begin{matrix} K \\ H \end{matrix}\right\} O_2 = \left.\begin{matrix} C_4H_3O_2 \\ K \end{matrix}\right\} O_2 + KCl + C_4H_4O_2 + 2HO.$$

Action of Chloracetine of Glycol on Butyrate of Silver.—Formation of Butyroacetate of Glycol.

Equivalent quantities of chloracetine and butyrate of silver were exposed in a balloon with a long neck to a temperature ranging between 100° and 200° C., till all the silver salt had been converted into chloride. The product was then digested with ether, filtered, and the filtered liquor submitted to distillation. As soon as all the ether had been driven off, the thermometer rose rapidly to 180°, and between that temperature and 215° almost the entire quantity passed over. This was fractioned, and the portion distilling between 208° and 215° was set apart for analysis. The numbers obtained lead to the formula $\left.\begin{matrix} C_4H_4 \\ C_4H_3O_2 \\ C_8H_7O_2 \end{matrix}\right\} O_4$, as will be seen from the following percentage table :—

	Theory.	Experiment.	
		I.	II.
C_{16}....	55·17	54·31	55·58
H_{14}....	8·04	8·20	7·97
O_5....	36·79	..	..
	100·00		

I also made a determination of the acids by heating a weighed quantity of the ether with hydrate of baryta in the usual manner. The quantity of sulphate of baryta obtained indicated 2·2 equivalents of acid for one equivalent of the substance analysed. The excess of acid was probably owing to the presence in the ether of a trace of free butyric acid. The following equation will explain the reaction which causes the formation of this compound:—

$$\left.\begin{matrix} C_4H_4 \\ C_4H_3O_2 \\ Cl \end{matrix}\right\} O_2 + \left.\begin{matrix} C_8H_7O_2 \\ Ag \end{matrix}\right\} O_2 = \left.\begin{matrix} C_4H_4 \\ C_4H_3O_2 \\ C_8H_7O_2 \end{matrix}\right\} O_4 + AgCl.$$

In many reactions chlorine replaces, and is replaced by, $H+O_2$; in this it is replaced by the group $C_8H_7O_2$ (equivalent to one atom of hydrogen) $+O_2$.

This ether, which I may call butyroacetate of glycol, has a bitter pungent taste. It is insoluble in water, but soluble in alcohol. It is specifically heavier than water. It is a very stable body,—solution of potash, even when boiling, effecting its decomposition with difficulty.

I have no doubt that many analogous compounds may be prepared in the manner I have just described.

Action of Chloracetine of Glycol on Ethylate of Soda.

In the hope of forming a compound intermediate between diacetate of glycol and diethylglycol, I resolved to try the action of chloracetine on ethylate of soda, thinking that probably the body in question might be generated by the following reaction:—

$$\left.\begin{matrix} C_4H_4 \\ C_4H_3O_2 \\ Cl \end{matrix}\right\} O_2 + \left.\begin{matrix} C_4H_5 \\ Na \end{matrix}\right\} O_2 = \left.\begin{matrix} C_4H_4 \\ C_4H_3O_2 \\ C_4H_5 \end{matrix}\right\} O_4 + NaCl.$$

In order to settle this point, I exposed equivalent quantities of these bodies in a sealed balloon to the temperature of a water-bath for about two hours. My expectations, however, were not realized. On opening the balloon, I found that the reaction had proceeded too far, acetic ether having been formed along with the chloride of sodium.

Action of Hydrochloric and Butyric Acids on Glycol.—Formation of Chlorbutyrine of Glycol.

This compound is prepared in the same manner as its homologue, namely by transmitting a stream of dry hydrochloric acid gas through a mixture of equivalent quantities of butyric acid and glycol, maintained at the temperature of 100° C. As soon as the reaction is finished, the product is well washed with water, dried by means of chloride of calcium, and distilled. The greater part passes over between 160° and 182°. This must be rectified, and the quantity distilling between 175° and 182° collected apart. This gave, on analysis,

results agreeing with the formula $\left.\begin{matrix}C_4H_4\\C_8H_7O_2\end{matrix}\right\}O_2$, as will be seen from the following table:—

	I.	II.
C_{12} .... 47·84	47·76	..
H_{11} .... 7·30	7·31	..
O_4 .... 21·28	..	..
Cl .... 23·58	..	23·88

The reaction, to which the formation of this body is due, may be thus explained:—

$$\left.\begin{matrix}C_4H_4\\H_2\end{matrix}\right\}O_4+\left.\begin{matrix}C_8H_7O_2\\H\end{matrix}\right\}O_2+HCl=\left.\begin{matrix}C_4H_4\\C_8H_7O_2\end{matrix}\right\}O_2+4HO.$$

Chlorbutyrine of glycol, as I may call this compound, has a pungent and somewhat bitter taste. It boils at about 190°. Its specific gravity at zero is 1·0854. It is insoluble in water, but freely soluble in alcohol. It is decomposed with difficulty by a boiling solution of potash, but readily by solid potash,—chloride of potassium, butyrate of potash, and oxide of ethylene, being formed.

I have ascertained that acetobutyrate of glycol, the ether I have already described, can be prepared from this body as well as from chloracetine, by exposing it to the action of acetate of silver. The process is the same as that I have already given, with this difference, that the reacting bodies must not be heated above 150° C. The ether prepared in this manner gave the following numbers on analysis:—

Theory.	Experiment.
C_{14} ....55·17	56·29
H_{14} .... 8·04	8·75
O_5 ....36·79	..

The quantity of this substance at my disposal was so small (the greater part of my product having been lost) that I could not purify it completely; hence the experimental numbers do not exactly accord with the theoretical.

Action of Hydrochloric and Benzoic Acids on Glycol.—Formation of Chlorbenzoate of Glycol.

A mixture of equivalent quantities of glycol and benzoic acid, previously fused and powdered, was exposed to the action of dry hydrochloric acid gas for several hours, the mixture being maintained at the temperature of 100° during the action of the acid, as in the case of the former compounds. The product thus formed presented the appearance of a soft white solid, and contained a considerable quantity of uncombined benzoic acid. This was removed by agitating it with hot water, till, on cooling, it no longer became solid, but remained perfectly fluid. Finally it was dissolved in alcohol, and precipitated by water. The body thus prepared, and without being

distilled, was analysed, having been previously dried *in vacuo* over sulphuric acid. Another specimen, prepared in the same manner, at a different time, was also analysed, having, however, been previously distilled. During the distillation it was observed that not a drop of fluid passed over till the mercury had risen to 254°, and between that temperature and 270° the entire liquid distilled over. What passed over between 260° and 270° was collected separately; this was the portion analysed. The numbers obtained on analysis agree with the formula $\left.\begin{matrix} C_4 H_4 \\ C_{14} H_5 O_2 \end{matrix}\right\} O_2$, as the following table shows:—

Theory.	Experiment.		Portion distilled.
	I.	II.	
C_{18}.... 58·54	59·70	..	58·69
H_9.... 4·87	5·01	..	5·31
O_4.... 17·35	..	..	..
Cl .... 19·24	..	17·93	..
100·00			

The portion not distilled contained doubtless a trace of free benzoic acid, which would affect the carbon and chlorine, but not the hydrogen.

Chlorbenzoate of glycol, as I shall call this compound, has a pungent and somewhat bitter taste. It is insoluble in water, but freely soluble in alcohol and ether. Boiling solution of potash effects its decomposition with difficulty, solid potash readily, the reaction being the same as in the case of the analogous compounds.

Action of Hydriodic Acid on Glycol.—Formation of Iodide of Ethylene and Iodhydrine of Glycol.

Hydriodic acid gas is absorbed with great energy by glycol. A considerable quantity of heat is evolved during the passage of the gas, and the liquor becomes black and thick from the separation of free iodine. On removing the iodine by means of dilute potash, a mass of small white crystals is brought to light, which I at once suspected to be iodide of ethylene. To remove all doubt on this point, I submitted the crystals to analysis, having previously purified them by recrystallizing from boiling alcohol. The numbers obtained agree with the formula of iodide of ethylene:—

Theory.	Experiment.
C_4.... 8·51	8·73
H_4.... 1·42	1·78
I_2.... 90·07	..
100·00	

The reaction which causes the formation of iodide of ethylene may be thus explained:—

$$\left.\begin{matrix}C_4H_4\\H_2\end{matrix}\right\}O_4+2HI=C_4H_4I_2+4HO.$$

That the action of hydriodic acid on glycol should be different from that of hydrochloric acid is doubtless owing to the bond of union between hydrogen and iodine being much weaker than that between hydrogen and chlorine.

If, on the other hand, the temperature of the glycol be prevented from rising during the passage of the hydriodic acid gas, by surrounding the vessel containing it with cold water, a liquid product is obtained, which is coloured dark-brown by free iodine. This I have not as yet been able to discover any means of purifying, it being soluble in water, and decomposed by distillation. I believe, however, it is the compound corresponding to chlorhydrine of glycol $\left(\left.\begin{matrix}C_4H_4\\H\\Cl\end{matrix}\right\}O_2\right)$ discovered by M. Wurtz. A portion of this liquid, from which I had simply removed the free iodine, by agitation with mercury, gave, on analysis, numbers agreeing tolerably well with the formula of iodhydrine of glycol. After the analysis, however, I discovered that it contained a considerable quantity of iodide of mercury in solution. Another portion, from which I had removed the iodine by means of metallic silver, gave, on analysis, 11·1 per cent. carbon and 3·5 hydrogen, instead of 13·9 carbon and 3·0 hydrogen. After all, an analysis is not necessary to enable us to arrive at the composition of this body. The products formed by the action of potash on it furnish us with almost as convincing a proof of its composition as any analysis could do. They are iodide of potassium and oxide of ethylene.

Iodhydrine of glycol is soluble in water and alcohol, but insoluble in ether. It has no taste at first; after a time, however, it almost burns the tongue, it is so pungent. It is decomposed by heat into iodide of ethylene, and probably glycol. It acts with great energy on the salts of silver.

Action of Hydriodic and Acetic Acids on Glycol.—Formation of Iodacetine of Glycol.

A stream of hydriodic acid gas was conducted into a mixture of equivalent quantities of glacial acetic acid and glycol, the temperature of which was prevented from rising during the action of the gas. As soon as a portion of the liquid gave a considerable quantity of an oily precipitate on the addition of water, the passage of the gas was interrupted; for the prolonged action of the gas is apt to give rise to the formation of iodide of ethylene. The liquid thus obtained was well washed with very dilute potash, dried *in vacuo*, and analysed. The numbers obtained lead to the formula $\left.\begin{matrix}C_4H_4\\C_4H_3O_2\\I\end{matrix}\right\}O_2$, as

will be seen from the following table:—

	Theory.	Experiment.	
		I.	II.
C_8....	22·42	21·95	22·30
H_7....	3·27	3·31	3·50
O_4....	14·96	..	..
I	59·35	..	..
	100·00		

Iodacetine has a sweetish pungent taste. It is insoluble in water, but soluble in alcohol and ether. Its specific gravity is greater than that of water. It crystallizes in tables when exposed to cold. Heated with potash, it gives iodide of potassium, acetate of potash, and oxide of ethylene. It is readily decomposed by the salts of silver.

This compound can also be prepared with great facility by exposing monoacetate of glycol to the action of hydriodic acid gas. The liquid must be kept cold during the action of the gas, which should be interrupted as soon as the addition of water to a portion of it causes an abundant oily precipitate. The whole is then washed with dilute potash, and dried *in vacuo*. A specimen prepared in this manner gave, on analysis, 22·62 per cent. carbon and 3·43 hydrogen, instead of 22·42 carbon and 3·27 hydrogen.

I hope soon to have an opportunity of studying these iodine compounds more particularly.

Action of Anhydrous Acetic Acid on Glycol.—Formation of Monoacetate of Glycol.

A mixture of equivalent quantities of anhydrous acetic acid and glycol was heated in a sealed tube for several hours at a temperature not exceeding 170° C. On opening the tube, and submitting its contents to distillation, it was observed that the mercury remained stationary for a considerable time at about 120°, the point of ebullition of glacial acetic acid, and then rose rapidly to 180°, between which and 186° the remainder of the liquid passed over.

This was analysed, and proved to be pure monoacetate of glycol.

Theory.	Experiment.
C_8.... 46·15	46·02
H_8.... 7·69	7·80
O_6.... 46·16	..
100·00	

The following equation will explain the reaction which takes place between the acid and the glycol:—

$$\left.\begin{matrix}C_4H_4\\H_2\end{matrix}\right\}O_4+\left.\begin{matrix}C_4H_3O_2\\C_4H_3O_2\end{matrix}\right\}O_2=\left.\begin{matrix}C_4H_4\\C_4H_3O_2\\H\end{matrix}\right\}O_4+\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2.$$

The foregoing experiments were performed in the laboratory of M. Wurtz.

THE CHEMICAL GAZETTE.

No. CCCCVI.—September 15, 1859.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Isomerism of Organic Compounds. *By* F. Beilstein.

By treating aldehyde with perchloride of phosphorus, Wurtz obtained an organic chloride, $C^2 H^4 Cl^2$, which he has named provisionally chloride of æthylidene. This body is isomeric with Dutch liquor. I have undertaken some experiments with the view of ascertaining whether this body is identical or isomeric with Regnault's chloride of chlorinated æthyle. On comparing the properties of chloride of æthylidene with those of chloride of chlorinated æthyle, I have been surprised with the concordance which exists between them; thus the boiling-point of chloride of æthylidene is 136°—138° F., and that of chloride of chlorinated æthyle 147° F., whilst chloride of æthylene boils at 180°·5 F.

The density of chloride of chlorinated æthyle is 1·174 at 57°·4 F.; that of chloride of æthylidene 1·189 at 39°·7; and that of chloride of æthylene 1·256 at 53°·6 F.

This agreement was confirmed by all the experiments which I made with the two bodies, so that it is very probable that chloride of æthylidene is nothing but chloride of chlorinated æthyle, the two bodies being identical.

The difference between the boiling-points (136°—138° and 147° F.) must be attributed to the unavoidable presence of more highly chlorinated and less volatile products in the chloride of chlorinated æthyle. The latter does not present a fixed boiling-point. The following is an analysis of portions distilled between 132° and 150° F.:—

	Found.	Calculated.
C	23·89	24·24
H	4·36	4·04

By the action of chloride of æthylidene upon æthylate of soda, Wurtz and Frapolli obtained chloride of aldehydene*. I have re-

* Chem. Gaz. vol. xvi. p. 461.

peated this experiment with chloride of chlorinated æthyle, and obtained exactly the same chloride of aldehydene. In this reaction there is formed a small quantity of acetal, the presence of which has also been remarked by Wurtz and Frapolli in the reaction of chloride of æthylidene upon æthylate of soda. The odour of the two bodies is the same. When heated in a sealed tube in the oil-bath with an alcoholic solution of acetate of potash, chloride of chlorinated æthyle is decomposed into muriatic acid and into chloride of aldehydene. Chloride of æthylidene behaves in the same way.

Alcoholic ammonia also decomposes the two bodies into muriatic acid and chloride of aldehydene.

The silver-salts have no action upon the two chlorides.

Chloride of æthylidene is readily attacked by chlorine. When it is exposed to the sun with the latter, crystals of sesquichloride of carbon, identical with that obtained from chloride of chlorinated æthyle, are soon formed.

If this coincidence takes place generally, which must be confirmed by other experiments, and which I propose to investigate in other series, we may suppress several series of isomeric compounds.

There is in chemistry a considerable number of compounds possessing the same composition, and endowed with different properties. Every day new ones are obtained. They are called isomeric compounds. We often find the explanation of isomerism in differences of constitution or of derivation. Sometimes this explanation escapes us, and we ascertain a difference of properties in bodies possessing the same composition without being able to explain these facts. The object of science is to cause the disappearance of these cases of isomerism, or to reduce them to clear and exact notions concerning the constitution and the mode of derivation of the bodies called isomeric.—*Comptes Rendus*, July 18, 1859, p. 134.

On the Presence of Urea in the Chyle and in the Lymph.
By A. Wurtz.

Two years ago there was at Alfort a bull into the thoracic canal of which a fistula had been made. I had the idea of seeking urea in the chyle of the animal. I was led to this by the thought that the urea must originate, not in the capillary system of the blood-vessels as has sometimes been asserted, but in the intimate structure of all the tissues, wherever materials which have become unfit for life require to be carried off by respiratory combustion. If this were the case, it seemed to me that urea should be met with not only in the blood, where its presence has long been ascertained, but also in the lymph, and consequently in the chyle of the thoracic canal. It appears natural, in fact, that the lymphatic vessels assist in the absorption of the materials arising from the metamorphoses of the tissues in which the ramifications of those vessels are immersed.

The chyle of the bull above mentioned proved to be very rich in urea. I coagulated by heat about 600 grms. of this chyle, evaporated

the filtered liquid, treated the residue with absolute alcohol, evaporated the alcoholic extract, and exhausted it with æther. This left perfectly colourless crystals of urea, which was partially converted into nitrate.

This result led me to extend my investigations to the lymph itself. Having been enabled by the kindness of M. Colin to obtain lymph of the dog, cow, bull, and horse, I ascertained the presence of urea in it. It appeared to me to be interesting to compare the quantities of urea contained in the blood, the chyle, and the lymph of the same animal. For this purpose it was necessary to undertake some quantitative experiments, which were performed by means of a process founded upon a combination of the methods proposed by Liebig and Bunsen for the determination of urea.

In the following Table the numerical results of my experiments are brought together:—

Name of the animal.	Diet.	Quantities of urea in 1000 grms.		
		Blood.	Chyle.	Lymph.
Dog	Fed on meat	0·089	.....	0·158
Id.	Id.	.....	0·183	.....
Cow	Dry lucerne	0·192	0·192	0·193
Bull	Lucerne and rapecake	.....	0·189	0·213
Another bull	Rapecake, before rumination.	.....	.....	0·215
Ram	Usual diet: rumination suspended.	(arterial) 0·248	0·280	.....
Sheep	Do.	.....	0·071	.....
Horse	Do.	.....	.....	0·126 0·112

I should add, that having had the opportunity of analysing a certain quantity of true chyle collected on the course of the chyliferous mesenteric vessels and beyond the ganglia, I also ascertained the presence of a small quantity of urea therein. This is no doubt due to the mutations of tissues which take place in the walls of the intestine itself.—*Comptes Rendus*, July 4, 1859, p. 52.

On the Constitution of Lactic Acid. *By* H. Kolbe.

With regard to glycolic acid, lactic acid, and leucic acid, the author expresses the opinion that these bodies have the same constitution as Gerland's oxybenzoic acid, and must stand in the same relation to acetic acid, propionic acid, and capronic acid, as oxybenzoic to benzoic acid. All these acids, namely oxybenzoic, glycolic, lactic, and leucic acids, are produced, according to Kolbe, from the allied benzoic, acetic, propionic, and capronic acids by the substitution of 1 equiv. of peroxide of hydrogen for 1 equiv. of hydrogen. In the assumption that peroxide of hydrogen must in this case be regarded as a displacer of hydrogen, the author finds no difficulty; and he then represents the formulæ of these acids with

those of the primary acids and of the amide acids belonging to them, under the following rational formulæ :—

$HO.(C^2H^3)C^2O^2,O$	$HO.\left(C^2\left\{\begin{matrix}H^2\\H^2N\end{matrix}\right.\right)C^2O^2,O$	$HO.\left(C^2\left\{\begin{matrix}H^2\\HO^2\end{matrix}\right.\right)C^2O^2,O$
Acetic acid.	Amidoacetic acid (Glycocoll).	Oxyacetic acid (Glycolic acid).
$HO.(C^4H^5)C^2O^2,O$	$HO.\left(C^4\left\{\begin{matrix}H^4\\H^2N\end{matrix}\right.\right)C^2O^2,O$	$HO.\left(C^4\left\{\begin{matrix}H^4\\HO^2\end{matrix}\right.\right)C^2O^2,O$
Propionic acid.	Amidopropionic acid (Alanine).	Oxypropionic acid (Lactic acid).
$HO.(C^{10}H^{11})C^2O^2,O$	$HO.\left(C^{10}\left\{\begin{matrix}H^{10}\\H^2N\end{matrix}\right.\right)C^2O^2,O$	$HO.\left(C^{10}\left\{\begin{matrix}H^{10}\\HO^2\end{matrix}\right.\right)C^2O^2,O$
Capronic acid.	Amidocapronic acid (Leucine).	Oxycapronic acid (Leucic acid).
$HO.(C^{12}H^5)C^2O^2,O$	$HO.\left(C^{12}\left\{\begin{matrix}H^4\\H^2N\end{matrix}\right.\right)C^2O^2,O$	$HO.\left(C^{12}\left\{\begin{matrix}H^4\\HO^2\end{matrix}\right.\right)C^2O^2,O$
Benzoic acid.	Amidobenzoic acid.	Oxybenzoic acid.

In these formulæ glycolic and lactic acids appear to be derivatives of acetic and propionic acids. If this view be correct, the former acids must be preparable from the latter, and these again convertible into the former. The author remarks that by the electrolysis of acetic acid acidulated with sulphuric acid, he has obtained an acid which appears to be nothing but oxyacetic acid.

In a previous article* it is also shown that propionic acid may be regenerated from lactic acid, and there is no doubt in the author's opinion that oxyacetic and oxycapronic acids may be converted into acetic and capronic acids. As regards lactic acid, Wurtz has lately given this acid the formula $C^6H^6O^6$, and described it as a bibasic acid. Wurtz also prepared chlorolactyle by treating lactate of lime with perchloride of phosphorus.

The author concluded that the compound described by Wurtz as chlorolactyle, $C^6H^4O^2,Cl^2$, has a different constitution from that expressed by this formula. He regards chlorolactyle as perchloride of chloropropioxyle, $C^4\left\{\begin{matrix}H^4\\Cl\end{matrix}\right.\Big\}C^2O^2,Cl$, a compound homologous with perchloride of chloracetoxyle, $C^2\left\{\begin{matrix}H^2\\Cl\end{matrix}\right.\Big\}C^2O^2,Cl$. He is of opinion that the conversion of lactic acid into this perchloride of chloropropioxyle by the treatment of its lime-salt with pentachloride of phosphorus takes place in accordance with the following equation :—

$$CaO.\left(C^4\left\{\begin{matrix}H^4\\HO^2\end{matrix}\right.\right)C^2O^2,O+2PCl^5$$

Lactate of lime.

$$=\left(C^4\left\{\begin{matrix}H^4\\Cl\end{matrix}\right.\right)C^2O^2,Cl+2PO^2Cl^3+CaCl+HCl;$$

Perchloride of chloropropioxyle.

* Page 206 of the present volume.

and also that the chlorolactic æther of Wurtz is chloropropionate of oxide of æthyle, $C^4 H^5 O . \left(C^4 \left\{ \begin{matrix} H^4 \\ Cl \end{matrix} \right) C^2 O^2, O$, produced in accordance with the equation

$$\left(C^3 \left\{ \begin{matrix} H^4 \\ Cl \end{matrix} \right) C^2 O^2, Cl + C^4 H^5 O . HO = C^4 H^5 O . \left(C^4 \left\{ \begin{matrix} H^4 \\ Cl \end{matrix} \right) C^2 O^2, O + HCl.$$

Perchloride of chloropropioxyle. — Alcohol. — Chloropropionate of oxide of æthyle.

The author induced Dr. Ulrich to make some further experiments upon the nature of chlorolactyle, the results of which, in the author's opinion, confirm his views.

The author then proceeds to a consideration of the glycols discovered by Wurtz, and of their products of oxidation, and puts forward his views upon glyoxal, glyceric acid, and aldehydes, with regard to which we must refer to the original.—Liebig's *Annalen*, cix. p. 257.

On Melampyrite. *By* W. Eichler.

The decoction of the herb of *Melampyrum nemorosum*, evaporated to the consistence of a syrup, deposits, as noticed by Hünefeld, a crystallizable body on cooling, which, from its properties, stands between gum and sugar. The author first prepared this body by Hünefeld's process, and afterwards found that it is best obtained by the following process:—

The decoction of the herb is mixed with milk of lime until a strong alkaline reaction is produced; it is then boiled, filtered, evaporated to a small volume, and mixed with muriatic acid until the reaction is slightly acid. During the cooling and the further evaporation of the mother-liquor melampyrite crystallizes, and may be readily obtained pure by recrystallization from water.

It seemed probable that this body might also occur in other Scrophulariaceæ; the author's experiments upon this point confirm this, especially as regards *Scrophularia nodosa* and *Rhinanthus crista galli*.

Melampyrite crystallizes in colourless, transparent, rhombic crystals, which are usually united to form crusts. It is inodorous, has a less sweet taste than sugar of milk; with solutions of equal strength of melampyrite and sugar of milk in water, the former appears to have a sweeter taste. Specific gravity $=1{\cdot}466$ at 59° F. It is readily soluble in boiling water. When a hot saturated solution was exposed for 2 days to a temperature of 59° F., the greater part of the melampyrite separated in a crystalline form; 1 part of melampyrite dissolves in 25·5 parts of water at 59° F., and in 1362 parts of alcohol of spec. grav. 0·825 at 59° F.

It is difficult of solution in acetone, chloroform, wood-spirit, and acetic æther, and insoluble in æther, benzine, turpentine, and naphtha.

When melampyrite is heated to 367° F., it fuses without loss of

weight, forming a clear, colourless fluid, which on cooling solidifies in a crystalline form, often with cauliflower-like excrescences. If the fused melampyrite be dissolved in boiling water, it crystallizes, apparently unchanged, on the cooling of the solution; for both this crystallized melampyrite and its compound of melampyrite and baryta possess the same crystalline form as the unfused melampyrite and the baryta compound prepared from it. When heated to 536° F., it becomes slightly brown, but solidifies in a crystalline form on cooling. If it be heated upon platinum-foil, it fuses and afterwards boils without becoming much embrowned (the vapours possess a slight odour similar to that of burnt sugar); it afterwards ignites, burns with a white flame and leaves very little coal, which burns away completely. The aqueous solution, mixed with yeast, does not ferment. When some grape-sugar had been added, and the fermentation of the sugar was completed, the fluid was filtered and evaporated. On its cooling unaltered melampyrite crystallizes from it. The solutions of both the unfused melampyrite and of that fused at 536° F. have no action upon polarized light.

The aqueous solution of melampyrite is not precipitated by the following reagents:—nitrate of silver, peroxide and protoxide of mercury; acetate of baryta, lime, copper, and lead; basic acetate of lead, perchloride of mercury, gold, and platinum; protochloride of tin; biniodide of potassium; lime and baryta-water. If melampyrite be boiled for two hours with dilute sulphuric acid, then saturated with carbonate of baryta, boiled, filtered, and evaporated, all the melampyrite crystallizes unchanged. If melampyrite be boiled with solution of potash, the fluid remains colourless, and after neutralization with acetic acid, the melampyrite crystallizes again. When it is boiled with solution of potash and sulphate of copper, a clear blue fluid is obtained. Melampyrite boiled with solution of potash and peroxide of mercury, does not reduce the latter. When boiled with dilute sulphuric acid and bichromate of potash, it also undergoes no change.

The analysis of melampyrite gave—

C	37·669	37·637	38·056	12 =	72	37·697
H	7·821	7·902	7·761	15	15	7·853
O	..	..	..	13	104	54·450

Nitromelampyrite.—By the treatment of melampyrite with nitro-sulphuric acid, nitrated bodies are obtained. One of these compounds is oleaginous, another crystalline, soluble in alcohol and æther, and a third pulverulent, nearly insoluble in alcohol and æther. By the action of sulphuret of ammonium upon these nitro-compounds, compounds of melampyrite with oxide of ammonium are formed.

Compounds of Melampyrite with Bases.—Melampyrite combines with bases. Its compounds with the alkalies and alkaline earths are soluble in water; those with the oxides of the heavy metals are insoluble in water.

Melampyrite and Oxide of Ammonium.—This compound is obtained when the compound of melampyrite and baryta is decomposed by carbonate of ammonia. The solution of the baryta compound is boiled for some time with carbonate of ammonia, filtered from the carbonate of baryta, and evaporated. Limpid, straight, six-sided prisms are deposited, which lose no ammonia at 212° F. When triturated with hydrate of lime they evolve ammonia, and furnish ammonia and free melampyrite with acids. The crystals are readily soluble in water; the solution has an alkaline reaction.

Melampyrite and Potash.—If hydrate of potash be dissolved in alcohol, mixed with melampyrite and heated, a considerable quantity of the latter dissolves, and after long standing concentrical groups of needles of melampyrite and potash separate; these dissolve very readily in water, attract carbonic acid and moisture from the air, and finally become a mixture of melampyrite and carbonate of potash, which may be separated by crystallization. The compound of melampyrite and potash has an extremely caustic alkaline taste.

Melampyrite and Soda.—The behaviour of melampyrite towards soda is similar to that towards potash, but the compound is less soluble in alcohol, and crystallizes in very small thin needles.

Melampyrite and Baryta.—If hydrate of baryta melampyrite and water be heated together, a clear solution is obtained, from which the compound of melampyrite and baryta separates on cooling in the form of six-sided prisms with a pyramidal truncation of the terminal edges. It is readily soluble in water, especially when hot, difficult of solution in alcohol, but not precipitable by alcohol from its aqueous solution.

This compound loses 26·725 per cent. of water at 248° F., and contains 32·051 per cent. of baryta.

$C^{12}H^{15}O^{13}$	..	1	= 191·0	40·64
BaO	32·151	2	153·2	32·58
HO	26·725	14	126·0	26·797

Melampyrite and Lime.—Dilute milk of lime readily dissolves melampyrite, but the compound could not be obtained free from melampyrite or excess of lime.

With *magnesia* no compound could be obtained.

Melampyrite and Oxide of Lead.—If an aqueous solution of melampyrite be added to an ammoniacal solution of acetate of lead, a white precipitate is obtained, which, when washed with water free from carbonic acid, and dried at 212° F. in a current of hydrogen gas, forms a white powder. The composition of this body is $C^{12}H^{15}O^{13}+6PbO$.

Melampyrite and Oxide of Copper.—Solution of melampyrite gives a pale blue precipitate with ammoniacal solution of sulphate of copper. The precipitate, when washed with weak aqueous ammonia until all the sulphuric acid was removed, became green when dried at 212° F. Composition $C^{12}H^{15}O^{13}+6CuO$.

Melampyrite and Sulphuric Acid.—Melampyrite dissolves in concentrated sulphuric acid, forming a colourless fluid, which gradually

acquires a brown colour when heated. This, when diluted with water and saturated with carbonate of lead, furnishes, after filtration, a colourless fluid, which was evaporated at a very gentle heat, and then decomposed by sulphuretted hydrogen. The fluid filtered from the sulphuret of lead formed, when evaporated, a slightly yellowish syrup of an acid and somewhat bitter taste. When heated, it is decomposed, becoming black, and evolving sulphurous acid.

Melampyritosulphate of Baryta.—The crude melampyritosulphuric acid, diluted with water, saturated with carbonate of baryta, filtered from the sulphate of baryta formed, and evaporated at a very gentle heat, left a turpentine-like mass of melampyritosulphate of baryta, which dried very slowly even *in vacuo* at 104°—122° F. The residue was a cracked, gum-like, transparent mass, with a scarcely perceptible yellowish tinge, readily soluble in water, insoluble in alcohol, and precipitable by alcohol from the aqueous solution in the form of a turpentine-like mass. At 212° F. it is decomposed into sulphate of baryta and free sulphuric acid, which on its part exerts a decomposing action upon the organic compound; sulphurous acid is evolved, and the residue becomes black. Analysis:—

$C^{12}H^{12}O^{10}$	..	1	=164·0	25·876
BaO	36·454	3	229·8	36·257
SO^3	37·792	6	240·0	37·867

Melampyritosulphate of Lime is prepared in the same way as the baryta salt; it is not precipitable by alcohol from the aqueous solution, but in other respects resembles the baryta salt, except that it dries still more slowly. The solution is not precipitated by nitrate of silver, protonitrate of mercury, or basic acetate of lead.

Melampyrite belongs to the glucosides, and approaches most closely to mannite. It is especially distinguished from the latter by the circumstance, that whilst a hot saturated alcoholic solution of mannite solidifies completely on cooling to form an asbestos-like mass, the similar solution of melampyrite only deposits a few clear crystals on cooling.

From *sorbine* it is distinguished especially by its less solubility in water and by its behaviour with nitric acid, which only furnishes oxalic acid with sorbine, and also by the brown colour acquired by a solution of sorbine in potash when heated. *Inosite* is sufficiently distinguished by the 16·7 per cent. of water of crystallization which it loses at 212° F., and by the change of colours produced by frequently repeated heating in the solution mixed with tartrate of copper and potash. *Quercite* only melts at 455° F., furnishes an uncrystallizable compound with baryta, and only gives oxalic acid when heated with nitric acid. *Phycite* fuses at 233°·6 F., and begins to boil at 320° F.; with sulphuric acid it furnishes a conjugate acid which gives a crystallizable salt with baryta; when heated with nitric acid it furnishes oxalic acid. *Dulcine* (dulcose) is distinguished by 9 per cent. of water of crystallization, which escape from it at a temperature of a few degrees above 374° F.—Buchner's *Neues Repert.* vii. p. 529.

On the Action of the Hydrated Alkalies upon the Nitric Æthers. *By* M. Berthelot.

In general the hydrated alkalies decompose the æthers and reproduce alcohol; this is one of the characteristic properties of that class of bodies.

The equation which represents this metamorphosis has often been compared to the precipitation of a hydrated metallic oxide by an alkali. But the metallic oxide is sometimes precipitated in an anhydrous state. From the fact that hydric æther, C^4H^5O, and alcohol, $C^4H^6O^2$, present the same difference of formulæ which distinguishes an anhydrous metallic oxide from a hydrated one, it may be supposed that the compound æthers might, under certain circumstances, furnish hydric æther instead of alcohol.

This was observed by the author to be the case four years since in the reaction of hydrated potash upon hydrobromic æther; but he has recently observed the same formation of a hydric æther in the reaction of the hydrated alkalies upon certain æthers formed by an oxacid, namely the nitric æthers.

The phænomenon is peculiarly distinct with methylonitric æther. It is only necessary to place a certain quantity of this æther in a pure state, a little water and a fragment of potash in a graduated test-tube reversed over mercury; in two or three days an evolution of gas commences and continues for several weeks. This gas is methylic æther, C^2H^3O:—

$$C^2H^3O, NO^5 + KO = C^2H^3O + NO^5, KO.$$

The proportion found was equal to $\frac{5}{6}$ths of the theoretical quantity. The last sixth is probably represented by methylic alcohol.

This experiment was repeated with ordinary nitric æther. This presents a greater resistance, and furnishes, according to circumstances, sometimes ordinary æther, sometimes alcohol. If the alkali be very dilute, the reaction effected at 212° F. in a sealed tube is still incomplete at the end of thirty-five hours; it only furnishes alcohol. But with solid potash, ordinary alcohol, ordinary æther, and a great abundance of a brown humoid substance are obtained.

The formation of the ordinary æther is represented by the formula

$$C^4H^5O, NO^5 + KO = C^4H^5O + NO^5, KO.$$

Sulphurous æther only furnished alcohol.—*Comptes Rendus*, Aug. 1, 1859, p. 212.

ANALYTICAL CHEMISTRY.

On the Determination of Grape-sugar, Cane-sugar, and Dextrine in their mixtures. *By* J. G. Gentele.

The analysis of a mixture containing grape-sugar, cane-sugar, and dextrine, or only two of these substances, is founded upon the following facts:—

1. A mixture of 1 part of ferridcyanide of potassium (the red prussiate) with half a part of hydrate of potash, dissolved in water,

has no action upon a pure solution of cane-sugar, either at ordinary temperatures or when heated to boiling. An extraordinarily small quantity of this reagent *gives the fluid a strong yellow colour*, and this colour is persistent.

2. The same reagent applied to a solution of *grape-sugar*, *loses its colour* very slowly in the cold, more rapidly between 122° and 140° F., but very rapidly between 140° and 176° F.

If a few drops of the solution of this reagent be poured into a solution of grape-sugar, heated to 140° F., and then well shaken, the yellow colour first produced very soon disappears (at 176° F. almost instantaneously). When the coloration is reproduced by the addition of a further portion of the reagent, it always disappears again as long as grape-sugar is present. Towards the end, the decolorization takes place more slowly, and is then facilitated by heating the fluid to 176° F. If the fluid retains its colour at this temperature, all the grape-sugar is destroyed.

This reagent is remarkably sensitive; the yellow colour which persists at last in consequence of the addition of an excess of the reagent, may be removed by a few drops of solution of grape-sugar.

3. *Dextrine*, prepared by roasting starch, *has no action* upon this reagent, even when it has been treated with muriatic acid under the same circumstances in which cane-sugar is converted into grape-sugar.

4. If a solution of cane-sugar in 40 times its weight of water, to which 55 per cent. of the weight of the sugar of concentrated muriatic acid has been added, be heated in the water-bath to 129°—131° F., all the cane-sugar is converted into grape-sugar. If this solution be then neutralized with carbonate of soda (an excess of which has no influence), it behaves like a solution of pure grape-sugar.

In order to apply these facts to the determination of grape-sugar, cane-sugar, and dextrine in their mixtures, it was first to be ascertained what quantity of ferridcyanide of potassium is necessary to decompose a certain weight of grape-sugar. Three experiments with a normal solution of ferridcyanide of potassium, proved that on an average it required 10980 milligrms. of the reagent for the decomposition of 1000 milligrms. of cane-sugar which had been converted into grape-sugar by means of muriatic acid, or 10·980 grms. of the salt to 1 grm. of cane-sugar.

A test-fluid was then prepared containing in 100 cubic centims. 10·980 grms. of ferridcyanide of potassium and 5½ grms. of hydrate of potash. On the other hand, 1 grm. of sugar was dissolved in 40 cubic centims. of water, and 250 milligrms. of concentrated muriatic acid were added thereto; the mixture was then heated on the water-bath for ten minutes to 129°—131° F. This solution was then neutralized with carbonate of soda, and gradually mixed with the test-fluid; of this 99·7 cubic centims. were decolorized, so that the sugar contained 99·7 per cent. of cane-sugar. By the optical test, the same sugar gave an amount of 99·75 per cent. of cane-sugar.

Thus the reagent proved to be very accurate. Towards the close of the operation, indeed, a slight yellowish colour made its appearance in consequence of the formation of a concentrated solution of ferrocyanide of potassium, but this is easily distinguished from that produced by $\frac{1}{10}$th cubic centim. of the test-fluid. This coloration is scarcely perceptible when the sugar is dissolved in double the above quantity of water; and also in tests which require a smaller addition of the test-fluid.

To examine a *mixture of cane-sugar and grape-sugar*, exactly 1 grm. of it is to be weighed off and dissolved in 40 cubic centims. of water; the solution is heated to 158° F., and then $\frac{1}{10}$th cubic centim. of the test-fluid is added from a graduated tube. If the colour disappears immediately (as with the syrups), a considerable quantity of grape-sugar is present, and entire cubic centimetres may then be added, until the colour slowly disappears at 158° F., when the addition of tenths of cubic centimetres is recommenced. If the colour produced by the last addition does not disappear in 15—20 seconds when shaken, the operation is completed, and the amount of sugar is then read off directly, the portion of the test-fluid which was not decolorized being deducted. From the cane-sugar indicated, the grape-sugar is calculated in centesimal parts x according to the equation

$$171 : 180 = n \text{ cubic centimeters} : x.$$

If the decolorization does not take place from the commencement (as with refined sugars), no grape-sugar is present; if it takes place slowly (as with raw sugar), only a small quantity of grape-sugar is present, and the testing must then be carried on very carefully, as already described for the completion of the operation.

On the other hand, in order to determine the cane-sugar contained in the mixture, 1 grm. of the same sample is again weighed off and dissolved in 40 cubic centims. of water; 250 milligrms. of concentrated muriatic acid are then added, and the mixture is heated in the water-bath for ten minutes to 129°—131° F.; when it has been neutralized with carbonate of soda, it is tested in the manner previously described. The per-centage of sugar is now found to be much greater than before, the cane-sugar being converted into grape-sugar. If the number of cubic centimetres of the test-fluid employed in the preceding test be deducted from the number now found, the difference gives the centesimal amount of cane-sugar.

The author found by experiments with mixtures of solutions of cane-sugar and grape-sugar, the amount of sugar contained in each being known, that they may be determined by the described process within $\frac{1}{10}$th per cent. Of the organic acids which may occur in syrups, he only found two which, even when combined with potash, are decomposed by the test-fluid, and therefore decolorize it like sugar,—these are oxalic and tartaric acids; on the other hand, citric acid, succinic acid, and acetic acid have no action on the test-fluid.

This method of determining cane-sugar and grape-sugar evidently rests upon the same principle as Fehling's test for sugar; if the latter be arranged so as to correspond with that described by the author, it gives a larger amount of grape-sugar when dextrine is present; and the difference between the results of the two tests is to be ascribed to dextrine, so that it becomes possible to distinguish the cane-sugar, grape-sugar, and dextrine in a mixture by a volumetric process.—Dingler's *Polytechn. Journal*, clii. p. 68.

New Process for detecting and determining the Amount of Iodine in the Dry way. *By* S. DE LUCA.

This process, and that communicated by the author to the Academy on the 5th of December, 1853, are founded on the power of bromine to decompose the iodides and set free iodine, without affecting the chlorides or bromides; in the former case he operated in the humid way, with a normal solution of bromine, but now in the dry way in closed vessels. The reaction commences at the ordinary temperature, and may be completed by the aid of a spirit-lamp.

Dry neutral iodide of potassium, or dry iodide of silver, is placed at the bottom of a glass tube closed at one end; and then a small glass bubble, drawn out and closed at the two extremities, and containing vapour of bromine, is slipped into the same tube. The air of the tube is replaced by dry carbonic acid, and it is then hermetically sealed. By shaking the tube two or three times the little bubble is broken, when the vapour of bromine comes in contact with the iodide which it decomposes, setting free iodine in the form of violet fumes, which condense on the cold part of the tube. When a larger quantity of iodide is to be decomposed, the iodide is placed in the small glass, and the tube is filled with vapour of bromine; the rest of the operation is the same as above described. On breaking the point of the tube under water, the latter rushes in and fills it, proving the complete absorption of the bromine.

Iodide of cyanogen is obtained by operating upon a dry mixture of iodide and cyanide of silver. If these bodies be placed in a tube filled with carbonic acid and enclosing a small glass containing bromine, the iodide of cyanogen produced on breaking the latter condenses in white silky tufts in the cold part of the tube. If the iodide of silver be in excess, violet fumes of iodine are observed.

This process may be applied to the detection of iodine in rain-water and other waters. The water is precipitated by nitrate of silver, the precipitate washed and dried, and then treated with bromine in a closed tube. Any chloride or bromide of silver which may be present are not decomposed by the bromine, which acts only on the iodide, setting free iodine.

The author has also applied the process to the quantitative determination of iodine, by the repeated action of small weighed quantities of bromine upon iodide of silver. When no more violet vapours are produced, or when the yellowish-red vapour of bromine makes its appearance, all the iodide is decomposed. The quantity of bromine

used gives, by calculation, the quantity of iodine set free; and this result may be checked by dissolving the liberated iodine in alcohol and testing it by a normal solution of sulphurous acid, and finally by converting the hydriodic acid formed into iodide of silver and determining the weight of this.—*Comptes Rendus*, Aug. 1, 1859, p. 214.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Coating of Engraved Copper Plates with Iron by the Galvanoplastic Process. *By* Dr. H. Meidinger.

The extremely remarkable application of the electrotype, which cannot fail to come into general use in the preparation of copper plates, and to diminish their cost considerably, has recently been repeated by a Frenchman of the name of Jacquin. Several years ago Prof. Böttger showed that iron could be easily separated by the galvanic current from a solution of 1 part of muriate of ammonia and 2 parts of sulphate of iron. It then presents the appearance of a silver-white speculum, and adheres quite firmly in thin layers upon well-cleaned metallic surfaces of copper, brass, &c.; but a thicker deposit separates again readily on bending. This perfectly pure iron precipitated by galvanism possesses quite different physical properties from that obtained by the process of smelting, which always contains intermixtures, although often in small quantities, of foreign bodies, especially carbon; that obtained by galvanism is as hard as steel and as brittle as glass. Upon this property depends Jacquin's discovery, which is at the same time the first technical application of iron deposited by galvanism.

Engravings on copper are well known to lose greatly in sharpness and expression after the first few hundred impressions have been worked off (these are consequently more highly prized and command a far better price in the market). This falling off of the plates is due to the constant friction and the great pressure to which they are exposed, by which the surface of the plate is gradually rubbed away, and the engraving becomes lighter until it may even disappear entirely.

The electrotype has indeed already enabled us to make any number of identical copies of an engraved copper plate; the process is, however, uncertain in unpractised hands and rather expensive; and moreover an electrotype copy of a copper plate will only furnish a far smaller quantity of fine impressions than the original plate of hammered copper, as its surface is much more easily worn away. For this reason there is no doubt that Jacquin's method of treating the surface of the original plate itself in so simple, certain, and cheap a way to enable it to furnish an almost unlimited number of equally good impressions, must be exceedingly welcome to all copper-plate engravers. This process consists, in brief, in coating the plate when completed with a very thin layer of galvanoplastic iron. In consequence of its extraordinary hardness, the latter

undoubtedly resists wear much better than the soft copper; and even should it suffer in the course of working, or become detached in spots, there is nothing to prevent the rest of the iron from being removed entirely by means of dilute sulphuric acid without the least injury to the copper plate, which may then be furnished with a new coating in the galvanic bath.

In order that the operation may be successful, some precautions must be observed. As in all cases where a galvanic deposit is to adhere firmly to a metallic ground (as in gilding and plating, coppering zinc and iron, &c.), a perfectly clean surface must be offered to the deposit of iron; the engraved copper plate must not be in the least greasy or oxidized. The grease which may be produced upon it by mere contact with the fingers, is best removed by means of a little solution of caustic alkali; a solution of carbonate of soda may also fulfil the object. To remove oxide, the plate is immersed in dilute sulphuric acid, so that at last it appears perfectly bright. It is then washed with water, and put immediately into the iron-bath. Here it is attached to the negative pole by means of a copper wire, and opposite to it, at a uniform distance of half an inch to one inch, is placed a plate of iron of the same size united with the positive pole. By means of a powerful battery (which, however, must never give rise to the formation of bubbles of hydrogen on the copper plate), a perfectly uniform coating of bright iron is obtained in a short time, from 5 minutes to a quarter of an hour. The prepared plate is then very quickly washed with pure water, and afterwards with a solution of carbonate of soda, dried with a fine cloth, and finally rubbed with a little oil or some other fatty matter in order to prevent any injurious effects of air and moisture; in fact the plate is now treated just like an engraved steel plate, which it exactly resembles. The excess of ink is said to rub off the surface of the iron much more readily than off copper, so that the work of the printer is shortened by about half the time, in other words, twice as many impressions may be obtained in the same time. If this prove true, it forms a further and very valuable advantage of the new process.

As regards the composition of the saline bath, the author still considers the method described by Böttger as the best. The preparation of the bath by Jacquin's method, by means of the electrical current itself, by dissolving an iron plate connected with the positive pole in the solution of muriate of ammonia, is tedious, expensive, and inadmissible even upon theoretical grounds. The bath is therefore made with 2 parts of commercial sulphate of iron and 1 part of muriate of ammonia, which are mixed together and treated with water until the whole is dissolved; 2 pounds of sulphate of iron and 1 pound of muriate of ammonia require about 4 litres of water, when the solution amounts to not quite 5 litres. If the solution is to be employed directly, it must be previously boiled with fragments of iron plate (or nails), in order to convert any peroxide of iron that may be contained in the sulphate into protoxide, as the former would injure the deposit of iron. The same end is attained by leaving the solution for several days in contact with metallic iron in closed vessels. It is also necessary after use to preserve the solution

in such a way that it may not readily combine with oxygen. The sign of its goodness is its pale green colour; it must on no account possess any yellowish tinge. The formation of yellowish-brown or even black flakes in the solution during the operation cannot be entirely prevented; they are separated by filtration when convenient, but have no unfavourable influence upon the formation of the deposit of iron, if the copper plate be moved slowly to and fro in the bath.

The best form of cell for the decomposition is a wooden trough, of the length and depth of the copper plate, and about 2 inches clear in width; it should be coated internally with wax or pitch. If the iron plate which serves as the positive pole and which dissolves during the operation in the same proportion that the iron is deposited upon the copper plate, and thus keeps the bath in a proper state, be fixed to one wall of the trough, it leaves sufficient space to allow the copper plate to be slightly vibrated. Such an arrangement is to be preferred in this case to the employment of a flat trough, which is advantageously used in the preparation of thick copper plates.

Daniell's battery produces a sufficiently strong current for the decomposition of the solution of iron, if the negative excitant (the copper cylinder surrounding the zinc) possesses about the same amount of surface as the engraved copper plate. If the latter be very large, two or three Daniell's elements may be employed.—Dingler's *Polytechn. Journal*, clii. p. 359.

Note on the Amalgamation and Gilding of Aluminium. *By* Charles Tissier.

In a note of the 15th June 1859, M. Cailletet announced that he had succeeded in amalgamating aluminium, by placing it in communication with the negative pole of a galvanic battery, and immersing it in mercury moistened with acidulated water or with nitrate of mercury, or by means of amalgam of sodium moistened with water. The author has repeated some of these experiments, and found that the amalgamation takes place with great intensity by means of the pile. If the leaf of metal be not too thick, it may be completely amalgamated, and then becomes very brittle.

He has succeeded in obtaining the union of mercury and aluminium simply by means of a solution of caustic soda or potash. When cleaned and moistened with an alkaline solution, aluminium is seized upon immediately by the mercury, which then forms a brilliant silvering on its surface.

The properties of the amalgam of aluminium are very remarkable. Under the influence of mercury it ceases to be a precious metal, and acquires the properties of an alkaline-earthy metal. When exposed to the air the amalgam instantly loses its lustre, becomes heated and oxidizes rapidly, becoming converted into alumina and metallic mercury. Water decomposes it with evolution of hydrogen, formation of alumina, and deposition of mercury. Nitric acid attacks it with violence.

The author attempted to employ the ready amalgamation of aluminium as a means of gilding and plating it, but its nearly instantaneous alteration in the air prevented this.

To gild aluminium 8 grms. of gold are dissolved in nitromuriatic acid, the solution is diluted with water, and left to digest till the next day with a slight excess of lime. The precipitate of aurate of lime and the excess of lime, when well washed, is treated at a gentle heat with a solution of 20 grms. of hyposulphite of soda in a litre of water. The filtered liquid is adapted for gilding aluminium in the cold, without the assistance of the pile; the metal is immersed in it after being cleaned by the successive action of potash, nitric acid, and pure water.—*Comptes Rendus*, July 4, 1859, p. 54.

PROCEEDINGS OF SOCIETIES.

Royal Society.

On the Behaviour of the Aldehydes with Acids. By A. Geuther, Esq., and R. Cartmell, Esq.

[Received June 8, 1859.]

The authors of this paper, with a view of obtaining a series of combinations homologous with those already obtained from glycol by Wurtz—viz. diacetate of glycol, $\left.\begin{matrix} C_4H_4 \\ C_4H_3O_2 \\ C_4H_3O_2 \end{matrix}\right\} O_4$, and the isomeric body of Geuther from common aldehyde, by the action of anhydrous acetic acid,—have subjected common aldehyde, acroleine, and oil of bitter almonds to the action of hydrochloric, hydriodic, and sulphurous acids.

I. *Acroleine,—Metacroleine.*

1. *Acroleine and Hydrochloric Acid.*

By acting on acroleine, $C_6H_4O_2$, with dry hydrochloric acid gas, a body is formed of the composition $C_6H_5O_2Cl$, resulting from a direct combination of one atom of aldehyde with one atom of the acid. This substance is insoluble in water, and can be washed with it in order to free it from any excess of acid or acroleine which may be still present. By drying, which can only be done over sulphuric acid at low temperatures, the body, for which the authors propose the name of hydrochlorate of acroleine, is obtained in a mass of white crystals, presenting a texture like that of velvet. It melts at 32° C. into a thick oil, having a smell of slightly rancid fat. It is readily soluble in alcohol or ether, on evaporation of which it remains behind as a thick oil. When boiled with water, it remains, as far as can be seen, unchanged. Dilute solutions of the alkalies appear not to act on it. Heated with solution of ammonia in a sealed tube at 100° C., it is decomposed, chloride of ammonium and acroleine ammonia being the result. It does not combine with bichloride of platinum when in solution in alcohol, and very slowly reduces boiling ammoniacal solution of nitrate of silver. Heated alone, it decomposes into acroleine and hydrochloric acid. By the action of concen-

trated hydrochloric acid acroleine is set free. Dilute sulphuric and nitric acids decompose it likewise, setting acroleine free. Heated with hydrate of potash it gives off hydrogen, and there distils at the same time an oily body, which solidifies into magnificent colourless crystals, analyses of which prove it to be an isomeric acroleine, for which the authors propose the name *Metacroleine*.

Metacroleine as thus obtained is insoluble in water, but is capable of being recrystallized from alcohol or ether. The crystals form very long needles, more especially when melted metacroleine before solidifying is allowed to flow about in a glass tube. They resemble very much in appearance crystals of acetamide, possess a peculiar aromatic smell, and have a taste at first producing a cooling and afterwards a burning sensation. They are lighter than water. They melt at about 50° C., becoming solid at about 45°C. Before melting they are somewhat volatilizable, on which account they can be distilled in the vapour of water. On being heated, metacroleine is changed into common acroleine. Dilute alkalies do not effect any change in this substance. By heating with mineral acids, common acroleine is set free. On leading dry hydrochloric acid gas over metacroleine in a bulb-tube, the metacroleine melts and combines with the acid, producing the already-named hydrochlorate of acroleine. From this behaviour, the authors believe the acrolein contained in the compound of hydrochloric acid to be metacroleine, and not common acroleine. If metacroleine be viewed as $C_{12}H_8O_4$, the formula of the hydrochloric acid compound would then be $C_{12}H_8O_4$, $2HCl$; and the formation of metacroleine may be assumed to take place according to the following equation, $C_{12}H_8O_4$, $2HCl+2KOHO=C_{12}H_8O_4+2KCl+4HO$. The evolution of hydrogen has been found to be the result of a secondary action.

2. *Acroleine and Hydriodic Acid.*

These substances act very violently on each other if the acid in the gaseous form be led into acroleine, producing a hissing noise, as when red-hot iron is plunged into water. The resulting substance is insoluble in alcohol, ether, acids, and alkalies. Bisulphide of carbon dissolves out a little free iodine. Heated alone, iodine is set free.

3. *Acroleine and Water.*

Acroleine mixed with two or three times its volume of water, and exposed to the temperature of boiling water for eight days, undergoes a gradual change. Acrylic acid is produced, and a resinous substance, soluble in ether, melting at about 60°, and becoming solid at 55°C. At common temperatures it is hard and brittle, like resin. The per-centage composition of this resin, on analysis, was found to be the same as that obtained by Redtenbacher, and named Disacrylic resin*, viz. carbon 66·6, hydrogen 7·4.

4. *Metacroleine and Hydriodic Acid.*

When dry hydriodic acid gas is passed over dry metacroleine, the latter melts, and changes into a heavy yellow solution, resembling in smell and appearance the hydrochlorate of acroleine. It can be

* Chem. Gaz. vol. i. p. 744.

washed with water, and appears at ordinary temperatures to solidify into crystals; placed over sulphuric acid to dry, it decomposes, becoming brown, and setting iodine free. From the analogy in its formation, this compound can be properly viewed as hydriodate of acroleine.

II. *Aldehyde.*

1. *Aldehyde and Hydrochloric Acid.*

Lieben found that by the action of hydrochloric acid on aldehyde, a body of the composition $C_8 H_8 O_2 Cl_2$ was produced, having a constant boiling-point of from 116° to 117° C.*

The authors confirm Lieben's statement as to the replacement of O_2 by Cl_2 in two atoms of aldehyde, and have further obtained a new combination, analysis of it giving the formula as $C_{12} H_{12} O_4 Cl_2$, in which two equivalents of oxygen are replaced by the same number of equivalents of chlorine in three atoms of aldehyde. By the action of water, this compound, like that of Lieben, is resolved into hydrochloric acid and aldehyde. By heat, it is broken up into aldehyde and the body $C_8 H_8 O_2 Cl_2$. The authors propose for it the name protoxychloride of aldehyde.

2. *Aldehyde and Hydriodic Acid.*

By the action of hydriodic acid on aldehyde a compound is produced that decomposes with water into the aldehyde and the acid again, on which account it could not be purified. On heating, it is suddenly decomposed at 70° C., leaving a black resinous residue, which on distillation gave off vapours of iodine. In its mode of formation it is analogous to the bodies produced by the action of hydrochloric acid on aldehyde.

3. *Aldehyde and Sulphurous Acid—Elaldehyde.*

Dry sulphurous acid gas led into anhydrous aldehyde in cold water is absorbed with great avidity, 11 grammes of aldehyde absorbing 19 grammes of the acid, whilst an increase of volume takes place. The absorption-coefficient of aldehyde for this acid was found to be 1·4 times greater than that of alcohol for the same, and seven times greater than that of water for it. No chemical combination appears to take place, as, on passing a stream of carbonic acid through the fluid at a slightly elevated temperature, almost all the sulphurous acid can be driven out again. If aldehyde, saturated with sulphurous acid, be left for about a week at ordinary temperatures in a well-stoppered bottle, it suffers in this time almost a complete change into a body for which the authors propose at present the name Elaldehyde. To obtain it pure, the fluid is mixed with as much water as is necessary to dissolve it up; the acid is saturated by degrees with chalk, and the fluid obtained is distilled so long as oily drops pass into the receiver. The common aldehyde is separated in a resinous form by digesting for some time with solution of caustic soda or potash. By repeated distillation, the elaldehyde can be obtained free from everything but a little water. Analysis gives the formula of this aldehyde as $C_4 H_4 O_2$. It is therefore isomeric with common aldehyde. As

* Chem. Gaz. vol. xvi. p. 215.

it was obtained in quantity by the foregoing method, its properties were further examined. Its boiling-point was found to be 124° C., and solidifying-point 10° C. Whilst solidifying it likewise starts into crystals, the melting-point of which is also 10° C. The aldehyde here described under the name Elaldehyde is identical with that of Weidenbush*. Its mode of production from common aldehyde is the same; its boiling-point likewise agrees with that of the aldehyde of Weidenbush.

The elaldehyde of Fehling the authors believe to be identical with that they have obtained, and also that obtained by Weidenbush. That which goes far to prove the identity of the two latter is their vapour-densities. That of Weidenbush's is given as 4·58, whilst that of Fehling's is 4·52; both are converted into common aldehyde by heating gently with dilute sulphuric acid, and both crystallize at low temperatures. The only material discrepancy between them is the boiling-point of 94° C. given by Fehling for elaldehyde, whilst Weidenbush gives the boiling-point of his aldehyde as 125° C.

III. *Oil of Bitter Almonds.*

1. *Oil of Bitter Almonds and Hydrochloric Acid.*

This acid does not combine with oil of bitter almonds. Experiments made in sealed tubes, heated first to 100° C., and afterwards to 200°, gave no signs of a combination having been effected.

2. *Oil of Bitter Almonds and Hydriodic Acid.*

Much better results can be obtained when hydriodic acid is allowed to act on oil of bitter almonds. The gas is absorbed, producing an increase of volume and of temperature, and at the same time a little water. At the end of the operation two layers appear, of a dark-brown colour. The upper one, which is about a sixth part of the quantity of the under one, consists of concentrated hydriodic acid, whilst the under one, a heavy oil, is a compound of iodine and oil of bitter almonds. To obtain the substance in a pure state, it was first washed well with water to remove excess of the acid; next treated with moderately strong solution of sulphite of soda, to remove any excess of oil; lastly, on washing with water, the salt was removed from it. It can be dried rapidly over sulphuric acid at a temperature not higher than 20° C. A higher temperature produces gradual decomposition. In the preparation of this substance, 6 grammes of oil of bitter almonds absorbed 11 grammes of hydriodic acid gas. Analyses of the substance lead to the formula $C_{42} H_{18} O_2 I_4$, which will be observed to be 3 atoms of oil of bitter almonds, in which $2(O_2)$ is replaced by $2(I_2)$. The authors propose for it the name Oxyiodide of Benzaldehyde. The substance thus obtained melts at 28° C., and solidifies at about 25° C. into almost colourless rhombic plates if rapidly cooled down. When in a liquid state, the crystals mostly occur in groups of long needles. The colour of the substance in a melted state is brownish yellow; at moderate temperatures, and on standing in the air, it becomes still

* Chem. Gaz. vol. vii. p. 34.

darker in colour. It possesses a smell very much resembling cress. It volatilizes at common temperatures, its vapour attacking the eyes powerfully. Its vapour at higher temperatures, when carried away by that of water, becomes more and more intolerable, producing a very inflammatory effect on the eyes and nose, which is more painful and permanent than that from acroleine. It is insoluble and sinks in water, but can be distilled in the vapour of it. Watery solutions of carbonates and sulphites of the alkalies do not act on it. Alcoholic solution of potash decomposes it by degrees on heating a little, producing much iodide of potassium, some benzoic acid, and an oily body that remains dissolved in the alcohol, which is not oil of bitter almonds. Alcoholic and watery solutions of ammonia change it slowly into iodide of ammonium and oil of bitter almonds. Boiled with solution of nitrate of silver, it yields iodide of silver, and a smell of oil of bitter almonds. Concentrated hydrochloric acid changes it by degrees, becoming brown; concentrated sulphuric acid dissolves it on heating, with the separation of iodine.

In conclusion, the authors remark that the action of hydrochloric acid on aldehyde may be regarded as consisting in the replacement of two equivalents of oxygen by two of chlorine in one, two, or three atoms of this body: thus,

		Aldehyde containing chlorine.		
1 atom of aldehyde	$C_4 H_4 O_2$	$C_4 H_4 Cl_2$		
2 „ „	$C_8 H_8 O_4$	$C_8 H_8 O_2 Cl_2$	Lieben's body.	
3 „ „	$C_{12} H_{12} O_6$	$C_{12} H_{12} O_4 Cl_2$	Protoxychloride of aldehyde.	

The action of hydriodic acid on oil of bitter almonds gives rise also to a body derived from 3 atoms of this aldehyde, in which $2 (O_2)$ is replaced by $2 (I_2)$.

3 atoms of oil of bitter almonds, $C_{42} H_{18} O_6$ — Oxyiodide of Benzaldehyde, $C_{42} H_{18} O_2 I_4$.

In the case of acroleine, the action of hydrochloric acid is different; it combines directly with it, no elimination of water taking place. If we conceive, however, that, in the action of this acid on common aldehyde, the water which is there produced is the effect of a further decomposition, then we may readily suppose that, if this further decomposition had taken place in the case of hydrochloric acid and acroleine, a body derived from two atoms of acroleine, and having O_2 replaced by Cl_2, corresponding to the second term in the combination of aldehyde and chlorine, would have been the result; thus—

2 atoms of hydrochlorate of acroleine—

$C_{12} H_{10} O_4 Cl_2 - 2(H O) = C_{12} H_8 O_2 Cl_2$, corresponding to the term $C_8 H_8 O_2 Cl_2$ in common aldehyde.

There is a curious connexion which may be mentioned, in this substitution of chlorine for oxygen in aldehyde, between the formula of these bodies containing chlorine, and those of the isomeric modifications of aldehyde.

THE CHEMICAL GAZETTE.

No. CCCCVII.—October 1, 1859.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On some Metamorphoses of Acetone and Acetic Acid.
By Dr. R. Fittig.

If sodium be put into acetone contained in a retort, as long as an action takes place, flakes of a dazzling white, gelatinous body are formed, and afterwards a thick paste, which acquires a reddish-brown colour, especially at the surface.

If this paste be submitted to distillation, a large quantity of undecomposed acetone first passes over, but in a little time numerous oil-drops make their appearance in the neck of the retort. The receiver is now changed, and the contents of the retort are distilled off with a considerable increased heat until they are nearly dry. The second distillate thus obtained furnished a considerable quantity of crystals imbedded in a thick oil, after standing for a longer or shorter time. These were repeatedly pressed between blotting-paper, and could be purified by recrystallization from a little boiling water. Out of this solution they separate in large, perfectly limpid, isolated, quadratic tables, which were sometimes obtained by the spontaneous evaporation of the solution, of the size of half a square inch. They contained water of crystallization, and lost their transparency by the escape of this in a few moments, frequently even whilst being pressed between paper; when they stood for some time over sulphuric acid, they acquired a perfectly effloresced appearance. Notwithstanding the readiness with which they give up their water of crystallization, a direct determination of the latter was impossible, because by standing over sulphuric acid the crystals themselves are soon completely volatilized. For analysis, therefore, they were only pressed repeatedly between paper, and then immediately burnt; their composition is expressed by the formula $C^6 H^{12} O^8$.

The author conjectures that this compound is another modification

of acetone with 6 atoms of water of crystallization, $C^6 H^6 O^2 + 6 HO$. The water of crystallization could not, however, be completely got rid of. The substance, both when dried over sulphuric acid and when crystallized from anhydrous æther, always retains water of crystallization; and the author convinced himself that the crystals acquire the water of crystallization during the decomposition of the acetone, and not during the recrystallization of the substance from water. The analyses of the substance with its full amount of water are as follows:—

C	32·2	32·4	33·1	6	= 36	32·1
H	11·5	11·6	11·5	12	12	10·7
O	..	..	..	8	64	57·2

These numbers therefore lead to the formula $C^6 H^{12} O^8 = C^6 H^6 O^2 + 6 HO$. The substance dried for 14 days over sulphuric acid gave on analysis—

C	60·8	6	= 36	62·1
H	11·5	6	6	10·4
O	..	2	16	27·5

The crystals, $C^6 H^6 O^2 + 6 HO$, fuse at 107°·6 F., boil at about 392° F., dissolve readily in alcohol and boiling water, with more difficulty in cold water, and still more sparingly in æther. Their crystallization from the aqueous solution is much assisted by putting in a crystal, and by strong refrigeration. They form no combinations with alkaline bisulphites; they are insoluble in a cold concentrated solution of bisulphite of soda, they dissolve in it when heated, but crystallize from it again unchanged on cooling.

The author has also prepared another compound, which is nearly related to the preceding. He enclosed anhydrous acetone with dry ammonia in a glass tube, and heated it for several days to 212° F. After the completion of the action, the contents of the tubes were submitted to distillation; the distillation was continued until the thermometer rose to 158° F., when the contents of the retort were placed in a shallow vessel, and left to evaporate spontaneously. After standing for several days there remained a thick, deep-brown syrup, which, when mixed with perchloride of platinum, only furnished chloride of platinum and ammonium.

When the author allowed the syrup to stand in the air for a still longer period, large, transparent, regular, quadratic tables were deposited, possessing the greatest resemblance to the crystals obtained by the action of sodium upon acetone and subsequent distillation, but distinguished therefrom both by their greater solubility in æther, and also, strikingly, by their not effloresceing in the air. For analysis they were pressed between paper, and recrystallized from anhydrous æther. The analysis gave—

C	61·8	6	= 36	62·1
H	10·8	6	6	10 3
O	..	2	16	27·6

This substance, therefore, has the composition of acetone, and is

possibly paracetone. The crystals obtained from acetone by sodium, were consequently this compound with 6 atoms of water of crystallization.

The crystals fuse at about 122° F., are readily soluble in water, alcohol, and æther, and when heated to 482° F. in closed tubes become converted into a yellow, thickly fluid oil, and not into ordinary acetone.

Action of Caustic Lime upon Acetone.—The author enclosed acetone with caustic lime, and left the mixture to stand for 2, 3, and 6 weeks. He then distilled it without any addition of water, and obtained from all three a fluid which was decomposable by fractional distillation into two bodies, namely Kane's oxide of mesityle ($C^{12}H^{10}O^2$), and a body of the formula $C^{18}H^{14}O^2$. This mixture boiled at temperatures ascending from 212° to 482° F.

Pure Oxide of Mesityle, $C^{12}H^{10}O^2$, is a colourless, limpid oil, smelling strongly of peppermint, and with a very burning taste. It burns with a brightly luminous flame, does not dissolve in water, but dissolves in all proportions in alcohol and æther. Its specific gravity at 73°·4 F. is 0·848; the observed vapour-density is 3·67, and its corrected boiling-point 267°·8 F. Its analysis gave—

	I.	II.			
C	73·1	73·2	12	72	73·4
H	10·3	10·4	10	10	10·2
O	..	..	2	16	16·4

Nitric acid, and especially a mixture of nitric and sulphuric acids, converts oxide of mesityle into a brown, tenacious, resinous mass, which is insoluble in water, but readily soluble in alcohol, and separates again from this solution in a brown and resinous form.

Chlorine acts violently upon oxide of mesityle, and forms with it a colourless oil which is heavier than water. In attempting to distil it after washing with water and drying over chloride of calcium, it was decomposed. The undistilled oil was therefore only washed with water, and placed under a bell-glass with fragments of potash; in a short time it acquired a brown colour. This oil furnished 45·4 per cent. of chlorine; if its composition had been $C^{12}H^8Cl^2O^2$, it must have contained 42·5 per cent. of chlorine.

Oxide of mesityle does not combine with alkaline bisulphites under any circumstances; it is therefore different from the isomeric Dumasine, which furnishes readily crystallizable compounds with these salts.

The second fraction, with a higher boiling-point (above 392° F.), which was obtained by the rectification of acetone treated with caustic lime, could be decomposed by continued fractional distillation into a fluid boiling between 410° and 428° F., and another boiling between 428° and 446° F. The analyses of the two fluids gave nearly the same results, namely,—

	C	H
that boiling between 410° and 428° F.....	77·6	10·2
„ „ „ 428° „ 446° F.....	78·0	9·8

corresponding with the formula $C^{18} H^{14} O^2$. From its properties this body appears to be identical with the phorone which is prepared from camphorate of lime, or at all events with that prepared by the distillation of grape-sugar with caustic lime.

The products formed by the action of the caustic alkalies upon acetone are of such a nature that their production from acetone may be explained by the separation of water from the latter, and are therefore of the same kind as the bodies obtained by the action of sulphuric acid upon acetone. According as more or less water is extracted in either way, different kinds of these products are formed.

The first member of this series is oxide of mesityle, or, if we suppose the xylite of Schweizer and Weidmann to be identical with acetone, perhaps the xylite-naphtha obtained by those chemists by the action of potash, to which they indeed give the formula $C^6 H^6 O^{1\frac{1}{2}}$, but the composition of which, according to Völckel, is $C^{12} H^{11} O^3$ ($=C^{24} H^{22} O^6$); whilst the last member is the hydrocarbon mesitylene, investigated by Kane, Cahours, Hofmann, and Maule. When arranged according to their boiling-points, the known bodies of this series stand in the following order:—

		Boiling-point.
Xylite-naphtha	$C^{24} H^{22} O^6 = 4$ Act. $- 2$ HO;	230°—248° F. (Völckel)
Oxide of mesityle	$C^{12} H^{10} O^2 = 2$ Act. $- 2$ HO;	267°·8 F. (Fittig)
Mesitylene	$C^{18} H^{12} = 3$ Act. $- 6$ HO;	311°—320° F. (Hofmann)
(Phorone?)	$C^{18} H^{14} O^2 = 3$ Act. $- 4$ HO;	410°—428° F. (Fittig)
Xylitole	$C^{24} H^{18} O^2 = 4$ Act. $- 6$ HO;	above 392° F. (Löwig and Weidmann).

Chlorine and Acetone.—Dry chlorine acts violently upon pure acetone in diffused sunlight, so that the vessel must be cooled during this treatment. The treatment with chlorine is continued until no more muriatic acid is produced, and the product has acquired a yellowish-green colour. The result is an oleaginous body of the composition $C^6 H^4 Cl^2 O^2$, which Kane had previously ascribed to it; it is Kane's mesitchloral, for which the author prefers the name of bichloracetone.

This oil, when purified, boiled at 250°·7 F. (corrected boiling-point); it is limpid, and of a penetrating odour, affecting the eyes strongly and exciting tears; it has a stronger caustic action than almost any other body, a drop placed upon the skin causing a deep and very painful wound, which does not heal for a long time. It is insoluble in water, but mixes in all proportions with alcohol and æther. Its spec. grav. is 1·236 at 69°·8 F., and the spec. grav. of its vapour =4·32, calculated 4·39.

Bichloracetone is decomposed by caustic alkalies, by hydrate of baryta, and even by dry gaseous ammonia; there is a strong evolution of heat, and chlorides are separated. By the employment of concentrated solutions of the alkalies brown fluids were formed, which, when evaporated on the water-bath, left an uncrystallizable, tar-like mass, nearly of a black colour. When treated with ammonia and separated from the muriate of ammonia formed, it also

furnished a dark-coloured thick mass. The analysis of bichloracetone gave—

	I.	II.		
C	29·1	29·7	6=36	28·4
H	3·6	3·7	4 4	3·1
Cl	56·2	55·4	2 71	55·9
O	..	..	2 16	12·6

Bichloracetone combines with alkaline bisulphites to form crystallizable compounds. By continued agitation with a concentrated solution of bisulphite of soda, it evolves heat, and forms a clear fluid, from which colourless, nacreous laminæ separate after it has stood for some hours. These are readily soluble in water, and possess an unpleasant odour of bichloracetone; they were analysed after pressure between blotting-paper and drying over sulphuric acid. The analysis gave 13·8 per cent. of sulphur, and 29·3 per cent. of chlorine, corresponding with the formula $C^6 H^3 Cl^2 NaS^2 O^6 + 3 HO$.

The author was unable to procure Städeler's pentachloracetone, $C^6 HCl^5 O^2$, obtained by the treatment of acetone with muriatic acid and chlorate of potash.

Nitroacetone.—The author has obtained a nitroacetone, insoluble in water by treating acetone with fuming nitric acid. This could not be dried by the introduction of chloride of calcium; it evolved much gas and was decomposed. Its analysis led to no probable formula, and sulphuret of ammonium produced with it no amide body, but deposited sulphur, and formed brown, tarry, uncrystallizable substances.—Liebig's *Annalen*, cx. p. 23.

On the Action of Iodide of Æthyle upon Benzoylanilide.
By A. Borodin.

A mixture of 1 equiv. of benzoylanilide with rather more than 1 equiv. of iodide of æthyle, heated for a few hours on the water-bath in a closed vessel, acquires a deep red colour, and becomes thickly fluid. At the ordinary temperature the reaction only takes place very slowly. The mass formed is washed quickly with a small quantity of weak alcohol, and dissolved in hot alcohol (of spec. grav. 0·875—0·848); the solution is then treated with animal charcoal. The solution filtered from the animal charcoal, when evaporated on the water-bath, leaves a resinous, cracked residue. 6 grms. of benzoylanilide furnish nearly 11 grms., whence it follows that 1 equiv. of iodide of æthyle reacts upon 1 equiv. of benzoylanilide.

The new body is perfectly insoluble in water, and scarcely soluble in ordinary æther. Weak alcohol only dissolves it with difficulty, but it dissolves very readily in strong alcohol. When heated in a test-tube the substance becomes soft, fuses, and boils, at the same time becoming decomposed, and giving off violet vapours of iodine. The solution of the body in alcohol is decomposed by oxide of silver, hydrated oxide of lead, and caustic potash. The corresponding

protiodide is formed, together with a new resinous substance free from iodine. Sulphuric acid dissolves the original compound when heated, but decomposes it at the same time; the solution becomes black, and evolves sulphurous acid and vapours of iodine. When exposed to the air in solution or in a moist state, the body acquires a green colour.

The analysis of the body dried at 212° F. gave 37·02 per cent. of iodine; the formula $C^{30}H^{16}NI$ requires 37·50 per cent.

This iodized substance, when treated with caustic potash in its alcoholic solution, furnishes iodide of potassium and a resinous body which sinks to the bottom when the solution is not too much diluted. The portion remaining in solution is then precipitated with water, and the iodide of potassium and caustic potash are removed by washing with water. This substance is then dissolved in alcohol and purified by fractional precipitation with water. It is, however, very difficult to obtain the body perfectly pure.

The substance thus obtained is resinous, soft, and viscous; it dissolves readily in æther, and with more difficulty in alcohol; it is perfectly insoluble in water. The alcoholic solution has a weak alkaline reaction. Sulphuric acid dissolves the compound when heated; when the heat is increased, the solution becomes black and is decomposed with evolution of sulphurous acid. Nitrate of silver forms a flocculent precipitate in the alcoholic solution of this body, which is rapidly decomposed and becomes black. When heated in a test-tube, the substance fuses and boils with decomposition; an oily fluid with a strong alkaline reaction distils off. This body also becomes green when exposed to the air, but in a considerably less degree than the original compound. The analysis gave 82·09 to to 82·99 per cent. of carbon, and 7·91 to 7·28 per cent. of hydrogen. The formula $C^{60}H^{32}N^2O^2$ requires 82·56 per cent. of carbon and 7·33 per cent. of hydrogen. If this body be treated with iodide of æthyle no further reaction is obtained.

From these experiments it follows that benzoylanilide is a tertiary amide, and must be regarded as a molecule of ammonia in which 2 equivs. of hydrogen are replaced by the biatomic group $C^{14}H^6$, and the third by the phenyle group,—

$$N\left\{\begin{matrix}H\\H\\H\end{matrix}\right. \qquad\qquad N\left\{\begin{matrix}C^{14}H^6\\C^{12}H^5\end{matrix}\right.$$

Ammonia. Benzoylanilide.

The product of the action of iodide of æthyle upon benzoylanilide represents a protiodide of ammonium in which 2 equivs. of hydrogen are replaced by the biatomic group $C^{14}H^6$, and the other two by phenyle and æthyle,—

$$N\left\{\begin{matrix}H\\H\\H\\H.I\end{matrix}\right. \qquad\qquad N\left\{\begin{matrix}C^{14}H^6\\C^{12}H^5\\C^4\ H^5.I.\end{matrix}\right.$$

The compound $C^{60} H^{32} N^2 O^2$ represents oxide of ammonium :—

$$\left\{\begin{matrix} NH^4 . O \\ NH^4 . O \end{matrix}\right. \qquad \left\{\begin{matrix} N(C^{14} H^6, C^{12} H^5, C^4 H^5) . O \\ N(C^{14} H^6, C^{12} H^5, C^4 H^5) . O. \end{matrix}\right.$$

The nitrate is obtained by double decomposition, when nitrate of silver (dissolved in alcohol) is added to a solution of the above-mentioned iodide. For the removal of the excess of the silver-salt, pulverulent chloride of sodium is afterwards added to the mixture. The solution filtered from the chloride and iodide of silver and evaporated on the water-bath leave a resinous residue, which is washed with water in order to free it from the soda-salt.

The nitrate is resinous and soft; it dissolves in alcohol, and is insoluble in water and æther.

The acetate is obtained from the preceding by double decomposition with acetate of potash ; nitrate of potash is separated. In its physical properties it resembles the nitrate.

Both compounds are decomposed by heat, and only acquire very little colour when exposed to the air; they were not analysed.

These compounds have much analogy with those formed under similar circumstances from hydrobenzamide, except that the latter are biatomic, as hydrobenzamide is derivable from two molecules of ammonia.—*Bull. de St. Pétersbourg*, xvii. p. 408.

On Thiacetic and Sulphobutyric Acids. *By* Dr. C. Ulrich.

Kekulé has described a thiacetic acid of the composition $C^4 H^4 S^2 O^2$, which he obtained by the action of sulphuret of phosphorus upon hydrated acetic acid. The author has made some further experiments upon this acid in Kolbe's laboratory, and prepared the sulphobutyric acid analogous to it.

For the preparation of thiacetic acid, the author mixed together equivalent proportions of powdered pentasulphuret of phosphorus and glacial acetic acid in a spacious retort; the neck of the retort was directed upwards and united with the lower end of a Liebig's refrigerating apparatus, and the mixture was then gently heated. Sulphuretted hydrogen was evolved, arising from a small quantity of water contained in the glacial acetic acid, and the mass at the same time frothed strongly. After the action had continued about two hours, the neck of the retort was turned downwards and united with the upper end of the Liebig's apparatus, when distillation was effected.

The distillate is reddish, and contains thiacetic acid, acetic acid, and sulphur. A tenacious black mass remains in the retort, consisting principally of fused sulphur and phosphoric acid. The distillate was fractionally distilled. The fraction boiling at 199°·4 F. is

Thiacetic Acid, $C^4 H^4 O^2 S^2$, a colourless fluid, soluble in water, especially when hot, and still more readily in alcohol; it has an unpleasant, penetrating odour, resembling acetic acid, and at the same time sulphuretted hydrogen. It is heavier than water, having a spec. grav. of 1·074 at 50° F., which approaches very closely to that of

hydrated acetic acid. It boils at 199°·4 F. (Kekulé), and distils over unchanged; it does not become solid at 1°·4 F. The last-mentioned property furnishes a simple means of obtaining thiacetic acid from the crude acid still containing acetic acid, by allowing it to freeze.

Its vapour-density, determined at 356° F., was found to be 2·465. The vapour-density calculated for 4 vols. would be 2·631. This difference is due to the fact that at this temperature the thiacetic acid was partially decomposed. When the author determined the vapour-density at 257° F., he found 3·04, consequently a higher value. In this respect, therefore, thiacetic acid behaves exactly like acetic acid.

If thiacetic acid be heated in a sealed tube to 356°—392° F., crystals of sulphur separate from the fluid. Chlorine decomposes thiacetic acid with formation of chloride of sulphur, muriatic acid, and perchloride of acetoxyle. Nitric acid of spec. grav. 1·34 has no action upon it at ordinary temperatures, but on the application of heat it causes a complete decomposition with explosion; fuming nitric acid has the same effect even in the cold. Concentrated sulphuric acid decomposes it with evolution of sulphuretted hydrogen and subsequently of sulphurous acid, at the same time that sulphur separates.

The author has prepared several salts of thiacetic acid. These are all more or less soluble in water and alcohol, and less stable than acetates; they are obtained by the solution of metallic oxides ɹcarbonates, and also by the mutual decomposition of thiacetate ſbaryta with metallic sulphates.

Thiacetate of Potash (Acetoxylsulphide of Potassium), $C^4 H^3 KO^2 S^2$, is readily soluble in water and alcohol. It bears a temperature of 212° F.

Thiacetate of Soda, $C^4 H^3 NaO^2 S^2 + HO$, is soluble in water and alcohol.

Thiacetate of Ammonia is obtained by conducting gaseous ammonia into thiacetic acid as free from water as possible. It forms beautiful, small, white crystals, which are extremely deliquescent.

Thiacetate of Baryta, $C^4 H^3 BaO^2 S^2 + 3HO$, forms colourless crystals of the orthorhombic system, resembling heavy spar.

Thiacetate of Strontia, $C^4 H^3 SrO^2 S^2 + 2HO$, forms colourless crystals belonging to the rhombic system, which bear a temperature of 248° F. without decomposition.

Thiacetate of Lime, $C^4 H^3 CaO^2 S^2 + 2HO$, forms colourless crystals, which lose their water of crystallization at 212° F.

The *Magnesia-salt* is a tenacious deliquescent mass.

The *Mercurial Salt* is obtained in the form of a white precipitate by treating the potash-salt with bichloride of mercury. This precipitate very soon becomes black, in consequence of the formation of sulphuret of mercury. The *silver-salt* is obtained in the same way; it becomes black and decomposed at the moment of formation. *Hydrated peroxide of iron*, digested with thiacetic acid, dissolves in considerable quantity. The solution has a somewhat greenish

colour, which is probably due to a reduction of the persalt to protosalt. Sulphur is not precipitated, but remains dissolved in the free thiacetic acid. When the fluid is gently heated, sulphuret of iron is thrown down. Solution of perchloride of iron, mixed with a solution of a thiacetate, gives a clear fluid, which gradually becomes turbid by the separation of a slight yellow precipitate. This takes place more rapidly with the aid of heat.

If aniline be mixed with thiacetic acid, sulphuretted hydrogen is evolved, and a crystalline paste is obtained; this is not thiacetate of aniline, but

Acetoxylanilide, $(C^4 H^3 O^2, C^{12} H^5, H)N$.

Sulphobutyric Acid, $C^8 H^8 O^2 S^2$, is obtained by the treatment of hydrated butyric acid with pentasulphuret of phosphorus. It boils at 266° F., and is a colourless fluid of an extremely repulsive, almost unbearable, and very persistent odour; it is sparingly soluble in water, but mixes more readily with alcohol; like thiacetic acid, it dissolves sulphur, and then acquires a yellowish colour.

Sulphobutyrate of Lead, $C^8 H^7 PbO^2 S^2$, is thrown down in the form of a white voluminous precipitate when solutions of the acid and of acetate of lead are mixed together. This precipitate is soluble in much hot water, and also in alcohol; on cooling, the salt crystallizes in small, colourless crystals.

Valerianic Acid also furnishes a sulphoacid corresponding with the two preceding; but no sulphobenzoic acid could be prepared from benzoic acid.—Liebig's *Annalen*, cix. p. 272.

On the Absence of Sugar in the Urine in Diabetes insipidus.

By R. V. Tuson*.

It has been asserted by some, but denied by others, that the urine of patients suffering from the disease formerly known as *diabetes insipidus*, but now called *chronic diuresis*, contains a peculiar sugar differing from glucose in properties, but convertible into that variety of sugar by boiling with dilute sulphuric acid.

A patient having the above-named disease, was admitted into Charing Cross Hospital under the care of Dr. Willshire, and I availed myself of the opportunity of collecting a considerable quantity of his urine for examination.

At the time of his admission into hospital this patient voided fifteen pints of urine daily, which had a pale straw-colour, and was perfectly transparent.

Its specific gravity varied from 1002 to 1006. From the very low specific gravity, one of the characteristics of the urine in *diabetes insipidus*, the presence of sugar was considered improbable. Nevertheless, as a minute quantity of sugar might exist, although not indicated by the ordinary tests when applied to the urine as passed, about six gallons of the urine were cautiously evaporated to a small bulk, and filtered. The filtered urine, both before and after boiling with dilute sulphuric acid, was most carefully and repeatedly

* Communicated by the Author.

tested for sugar,—not the slightest indication of that body was however obtained. A portion of the fresh urine was allowed to stand in a warm place, in order that torulæ might be developed, but none were detected.

Chemical Laboratory,
Charing Cross Hospital.

On the Direct Formation of Nitruret of Silicium.
By Professor Wöhler.

Silicium behaves towards nitrogen like boron and titanium; at a high temperature it extracts nitrogen from the atmosphere.

If a small Hessian crucible be filled with crystallized silicium, closed and placed in a larger crucible, with the interspace filled with powdered charcoal to retain the oxygen of the air of the furnace, and the whole apparatus, after the larger crucible has been provided with a luted cover, be exposed for about an hour to the strongest coke fire, the silicium is found, after cooling, to be covered with a light, bluish, readily separable, coherent, fibrous substance resembling mountain cork. This is white, and only coloured at the surface. By means of the microscope, it could be perceived that this dark superficial colour was due to innumerable dark pinchbeck-coloured crystals, which reposed upon warts of a finely crystallized, white substance. The composition of these metallic crystals could not be ascertained.

Both the cork-like and the bluish mass evolved ammonia when fused with hydrate of potash.

The bluish mass was ignited in dry chlorine, in order to obtain it free from silicium.

Nitruret of silicium is not decomposed by chlorine any more than nitruret of boron. The nitruret of silicium purified by chlorine, evolved ammonia still more abundantly with hydrate of potash.

If nitruret of silicium be heated to a strong red heat in a current of aqueous vapour conducted by carbonic acid gas passing through water at about 194° F., crystallized carbonate of ammonia is formed at the end of the tube in which the ignition is effected. This decomposition takes place but slowly, while the nitruret of silicium prepared from the chloride gradually decomposes water even at ordinary temperatures. In the moist state it soon begins to smell of ammonia.

Crystals of silicium, when heated to redness in moist chlorine, become converted into transparent pseudomorphs of silicic acid. Next to oxygen, silicium is the element most widely distributed in nature. As it is not oxidized in the dense state by oxygen gas even when brought to a white heat, it is remarkable that it does not occur free in nature, especially as it does not decompose water at ordinary temperatures. If we wished to give ourselves up to geognostic fancies, says the author, we might suppose that at that period in the formation of our planet, when the elements combined to form those compounds of which its crust and mountains now con-

sists, silicium entered into combination with nitrogen, and then the nitruret of silicium, while still red-hot, coming in contact with water, gave origin to silicic acid and ammonia. Thus would be produced the ammonia, by which on the first appearance of living organisms nitrogen would be introduced into them.—Liebig's *Annalen*, cx. p. 248.

On the Chemical Nature of Silk. *By* A. Vogel, Jun.

The following are the results of the author's memoir upon silk.

1. The centesimal composition of the fibroine of silk is—

C	49·99
H	6·88
N	19·03
O	24·10

These numbers correspond with the formula $C^{48} H^{38} N^8 O^{17}$.

2. When treated with ammonia, the solution of fibroine in nitric acid furnishes a yellow metamorphic product of the composition $C^{48} H^{38} N^6 O^9$.

3. In the series of products of the metamorphosis of fibroine by means of nitric acid we recognize the endeavours of this body to approach, in its proportions, more and more to those of its type, oxalic acid; during which, however, at the same time a portion of its carbon, escaping as carbonic acid, is returned to the domain of inorganic nature.

4. Whenever fibroine is thrown down as such from its solutions, its alteration not having gone too far, these precipitates exhibit a remarkable tendency to the filamentous form, so that a fibrous texture appears to be intimately interwoven with the nature of this body.

5. From its composition fibroine forms a culminating member in the whole series of the proteine bodies; on the one side of it are arranged the true proteines, as structures in course of metamorphosis in the organism, whilst on the other side we have the proteine bodies occurring in the organism as secreted structures.

6. The elementary analyses of silk-jelly showed that this body has not hitherto been obtained in a perfectly pure state.—Buchner's *Neues Repert.* viii. p. 1.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Preparation of Murexide on a large scale. *By* G. J. Braun.

Although the use of this beautiful dye-stuff is at present so much diminished, whilst in the autumn and winter of 1857–58 almost incredible quantities of it were produced and used, it is certainly still undecided that this body has lost its practical value; neverthe-

less history shows that the first industrial application of a chemical product is rarely the most perfect.

In the application of murexide in dyeing and printing stuffs, the arts have again furnished a proof of their great versatility, a preparation, which had previously been rare and difficult to produce, having been offered by hundredweights and at a cheap rate to the stuff printers.

The author describes the process for the preparation of murexide on a large scale. Murexide may be prepared directly from guano, and indeed without first isolating the uric acid; or the latter may be effected, and then the process for the preparation of murexide is altered. The former mode of preparation is attended by many troublesome operations, for which reason the author has always preferred to prepare uric acid first of all, and to obtain the murexide from this; the former process is, however, described as accurately as the latter.

I. *Preparation of Murexide from Guano.*

The selection of a good guano is the principal point as regards the cost of production of the murexide; the best sacks, that is the lightest samples, are to be selected, as these contain the most urate of ammonia. The author has always found the amount of this salt in guano to vary, and could never meet with a uniform sample; this indeed is to be ascribed to the mode of deposition of the guano, as a homogeneous mixture is not attempted at the point of shipment.

In true Peruvian guano there was never less than 5 per cent., or more than 15 per cent. of uric acid. The statements of some text-books that only 1 to 2 per cent. of uric acid can be obtained from guano, are due to the defects of the old modes of preparing uric acid.

To proceed regularly in the way to be described on the large scale, a great quantity of guano must be mixed together, in order to obtain a homogeneous raw material, to suit the ascertained proportions of the reagents.

In the first place, the guano is treated with muriatic acid, to dissolve the carbonate and oxalate of ammonia, to decompose and dissolve the carbonate and phosphate of lime and the phosphate of ammonia and magnesia, and also to separate the uric acid from its alkalies, and especially from ammonia. This treatment is best effected in a leaden kettle to which heat may be applied; in this muriatic acid of 12° B. is heated, and then an equal weight of guano (with the larger pieces previously powdered) is put in slowly. If the guano be added rapidly, the effervescence produced may readily cause it to run over; this is avoided by a gradual addition of the guano.

The mixture is then boiled for an hour, and emptied into wooden vessels, in which it is washed by decantation with water; this treatment with water is repeated until all the soluble saline parts have been removed from the sediment. The strong saline solution thus obtained may be employed in the manufacture of ammonia or as a manure.

The acidulated and washed guano is collected upon large filters, and thus further freed from water. The product obtained contains 42 to 45 per cent. of dry substance: 100 pounds of guano usually furnish 30 pounds of this dry body. This result varies very little, although the product contains more or less uric acid.

This product contains all the uric acid of the guano, mixed with sand, clay, gypsum, organic remains, and extractive matters; a portion of the guanine of the guano is also present in it, but a part of it is extracted by the treatment with muriatic acid.

According to his patent of May 6th, 1856, R. A. Brooman uses this impure dry uric acid, as he calls it, for the preparation of murexide, treating it, first of all, with nitric acid of spec. grav. 1·41, and then proceeding in the well-known manner. The author and several others, however, have not succeeded in this object by the method described by Brooman; a particular obstacle was presented by the voluminous body with comparatively so little uric acid, to the action of the strong nitric acid, without danger of failure and of too great expense, and the prescribed evaporation of the filtered solutions was still more difficult.

From the experiments made by the author in the summer of 1857, it appeared that a totally different course must be adopted in order to obtain certain, and consequently uniform results, and that the production of alloxane must take place first of all, in order that this may be converted into alloxantine, and this again into murexide.

Brooman's purification of guano with muriatic acid is, however, undoubtedly of great value, especially for the production of uric acid.

In order to obtain a solution of alloxane from the guano purified with muriatic acid, the author proceeds as follows:—

Five pounds of the guano, treated as above, is put whilst still moist into an earthenware bowl, and heated with $1\frac{1}{4}$ pound of muriatic acid of 24° B. to 122° F. (40° R.); it is then removed from the fire, and gradually mixed with constant stirring with 6 ounces of nitric acid of 40° B., care being taken that the temperature does not rise above $144\frac{1}{2}$° F., nor sink below $100\frac{3}{4}$° F. Peruvian guano of average quality, containing 8 per cent. of uric acid, requires the above-mentioned quantity of nitric acid; according to the larger or smaller quantity of uric acid contained in the guano, the proportion of the oxidizing agent varies.

The author has also effected the conversion of the uric acid contained in the purified guano into alloxane by means of chlorate of potash, but did not apply this process on a large scale on account of its expense. 12 pounds of moist purified guano, containing 5 pounds of dry substance, and in this 2 pounds of uric acid, were mixed with 4 pounds of muriatic acid, and heated to 122°—$133\frac{1}{4}$° F.; then $6\frac{1}{2}$ ounces of finely powdered chlorate of potash were introduced, and the whole was well stirred, the temperature being watched, as it should not attain 140° F. These quantities gave 12 ounces of alloxantine, which furnished 15 or 16 ounces of murexide. The mixture containing alloxane is diluted with an

equal weight of water, and filtered; this process is repeated twice. All the solutions are then collected and combined, and from this mixture the alloxane is precipitated in the form of alloxantine by means of a saturated solution of protochloride of tin.

This separation takes place very readily, and it may easily be ascertained how long protochloride of tin is to be added. When a little protochloride of tin is added to the clear solution and no fresh precipitate is formed, even after the lapse of a few minutes, all the alloxane is converted into alloxantine, and this is thrown down in consequence of its difficult solubility. An excess of protochloride of tin is to be avoided, because it forms a precipitate, although but a slight one, with any other organic bodies that may be present.

After the precipitate has settled quietly, which soon takes place, the supernatant brown fluid is drawn off, and the alloxantine washed with water, acidulated with muriatic acid, in order to avoid a decomposition of the tin-salt.

The alloxantine thus obtained is filtered, dried, reduced to a very fine powder, and then exposed to hot vapours of ammonia, by which pure murexide is produced.

The treatment with ammonia is best effected in an iron sand-bath covered with a cylindrical cover of tin, upon the bottom of which fine linen is stretched, on which the finely powdered alloxantine is laid. The ammonia is evolved in the sand-bath from sulphate of ammonia and hydrated lime.

The alloxantine must be laid upon the linen loosely and not too deeply, and the tin cover is kept open, in order to give free egress to the aqueous vapours produced, so that the preparation may not cake together in consequence of the accumulation of moisture in it by which the action of the ammonia would be prevented.

If for any reason the action of the ammonia be incomplete, the murexide obtained must be pulverized, and again treated with ammonia. An excess of ammonia is not only not injurious, but even advantageous.

II. *Preparation of Uric Acid from Guano.*

Brooman's treatment of guano with muriatic acid is very advantageous as a preliminary to the preparation of uric acid, because by its means not only do all the necessary parts of the raw material remain, but the preparation of the uric acid is materially facilitated. The uric acid is extracted from the washed residue of the guano after treatment with muriatic acid by boiling with a weak solution of caustic soda; a great part of the extractive matter is then precipitated by caustic lime, and the uric acid is thrown down from the clear decoction by means of muriatic acid. The details of the author's process are as follow:—

The mass obtained by the treatment of 200 pounds of guano with muriatic acid and washing the residue, is put into a copper kettle capable of containing 160 Winchester gallons, together with 120 gallons of water and 8 pounds of caustic soda; this mixture is heated to

boiling with constant stirring, and kept at that temperature for an hour; a lime-paste of 2—3 pounds of caustic lime is then added, the whole is allowed to boil for a quarter of an hour longer, then removed from the fire, and left quietly to clear in the kettle. In three or four hours the fluid is sufficiently cleared, so that it may be drawn off into another vessel by means of a siphon; in this the uric acid is precipitated, whilst the fluid is still warm, by means of a slight excess of muriatic acid. By this precipitation, whilst hot, the uric acid acquires a finer consistence, so that it settles more readily in the fluid, and may be easily washed and filtered. After filtration it is dried in warm air.

It is a remarkable circumstance in this process, that the lime is only employed after the action of the caustic soda, whilst hitherto both alkalies have been allowed to act simultaneously; in the latter case urate of lime is always formed, which requires a large quantity of water for its solution, so that, on a large scale, the solutions to be operated upon would be enormous in quantity; by the author's method, on the contrary, nothing but readily soluble urate of soda is formed, and the caustic lime, which fixes a great portion of the extractive matter, serves only to clear the fluid, for which purpose, and with the view of avoiding the formation of urate of lime, it is only employed in a proportion equivalent to the excess of caustic soda.

After the kettle has been emptied of its clear contents, the same quantity of water as before is run in upon the residue; then 5 or 6 pounds of caustic soda are added, and the previous treament is repeated, except that only 1 or 2 pounds of hydrate of lime are employed to clear the fluid.

After this second decoction the guano is in most cases entirely deprived of its uric acid; it is only with very good samples that a third boiling with a still smaller quantity of caustic soda and lime is required.

The final residue in the kettle, when dried, is still a good manure.

The uric acid thus obtained, is used by the author without further purification in the manufacture of murexide; it is yellow, and therefore not quite pure. In the preparation of murexide for dyeing purposes, a uric acid containing 3—5 per cent. of extractive matter is quite applicable, as these foreign matters are destroyed by the oxidation with nitric acid, and may then be extracted by water from the murexide formed.

III. *Preparation of Murexide from Uric Acid.*

As is known from the chemical text-books, uric acid is always first of all converted into alloxane by nitric acid. The proportion of uric acid and nitric acid which is necessary for this conversion must be previously ascertained; after numerous experiments the author adhered to the following process:—

Into $2\frac{1}{8}$ pounds of nitric acid of 36° B. $1\frac{3}{4}$ pound of uric acid is gradually introduced, for which purpose the following process is to be adopted.

The nitric acid is poured into a deep earthen basin, which is placed with its contents in a vessel of cold water, so that it floats upon the latter; at the same time precautions are adopted to enable the heated water to be replaced by fresh. The uric acid is now added gradually in small quantities to the nitric acid; more than 1 ounce must not be introduced at once, as otherwise in consequence of the reaction too great an amount of heat would be evolved, and a portion of the alloxane formed would be decomposed into products incapable of forming murexide, so that the uric acid employed in the formation of this alloxan would be entirely lost.

The uric acid is also to be only sprinkled upon the surface of the nitric acid, and the mixture is only to be stirred round with a porcelain spatula, after the uric acid is for the most part consumed; by proceeding in this way, the heat evolved is more rapidly carried off. A fresh portion of uric acid must never be introduced into the nitric acid until the temperature of the mixture has fallen at least to 90½° F. Subsequently the mutual action of the two bodies becomes weaker, and then it becomes necessary to stir up the uric acid added with the nitric acid, before the mixture has cooled to so low a temperature that the oxidation ceases, and must be reproduced by the application of a gentle heat. This, however, can only happen in winter.

The last portions of uric acid are no longer consumed by the temperature of 90½° F., which is also taken into consideration with the proportion of nitric acid selected. It is not advisable to operate with a larger quantity of uric acid and nitric acid than the above in a single earthen vessel, but in the manufacture on a large scale, a number of basins with the above-mentioned quantity of nitric acid in each are placed in a common cold water-bath. As a matter of course a good draught must be provided for getting rid of the fumes produced.

When cold, the mixture obtained forms a crystalline paste of alloxane, with uric acid, water, and a little free nitric acid; the yellow colour of the fluid is produced by the decomposition of the extractive matter, with which the uric acid employed was contaminated. The products of two elaborated portions (that is of 3½ pounds of uric acid and 4½ pounds of nitric acid) are now mixed in an enamelled iron pot, and this is placed upon a hot sand-bath, or upon a furnace covered with sand. With the aid of heat, the action of the dilute nitric acid contained in the mixture upon the uric acid still present produces a quantity of alloxantine; when the mixture which rises during the reaction has half-filled the pot, this must be removed from the furnace; and when the mixture has fallen (without being stirred), the vessel is replaced upon the sand-bath, when the mixture again rises, and the vessel must again be removed from the fire. At the third heating the danger of running over is no longer to be feared, and the temperature of the mixture is therefore allowed to rise to 248° F.; the vessel is then removed to a cooler spot of the furnace, and half a pound

of liquid ammonia of 24° B. is stirred in as quickly as possible. By this means the mixture is entirely converted into murexide.

After the introduction of the ammonia, the vessel is left standing for about two minutes more upon the hot place, and it is then removed for the purpose of cooling, after which the mixture is found to be converted into a dark reddish-brown tough paste. This consists principally of murexide, mixed with nitrate of ammonia, soluble brown extractive matter, &c. It forms the so-called *Murexide en pâte* of commerce.

To obtain the murexide in a purer state and dry, this paste is stirred up with water and filtered, and this is repeated until all saline portions and extractive matters are washed out. It is finally washed with weak ammonia. After the last filtration the product is dried in a drying chamber, when it forms the *Murexide en poudre* of commerce.

The author has made some experiments upon the use of murexide for lake colours and red dyes; these have partially succeeded.—Dingler's *Polyt. Journal*, clii. p. 193.

On the Fusion of considerable Masses of Platinum. *By* MM. Sainte-Claire Deville *and* Debray.

The authors state that by the combustion of coal-gas with oxygen by means of the apparatus already described by them (Comptes Rendus, xliv. p. 1101), and since greatly improved, they have succeeded in fusing a mass of 11·59 kilogrms. of platinum in vessels of coke, and that there is nothing to prevent much larger quantities being fused by this apparatus. According to them, 1 kilogrm. of platinum requires, according to its purity, 60 to 100 litres of oxygen for its fusion, and 1 kilogrm. of the ore requires 600 to 900 litres of that gas for its complete treatment; 1000 litres of oxygen, prepared from brown oxide of manganese cost, 4·50 francs. In this way they have also prepared triple alloys of platinum, rhodium, and iridium, which greatly exceed mere platinum in hardness and resistance to acids, &c.

They also fused osmium, and obtained it in a very hard and shining state, capable of scratching glass; its spec. grav. in this state is 21·4, which the authors regard as the highest of any metal, iridium, according to them, only possessing a spec. grav. of 21·15.—*Comptes Rendus*, xlviii. p. 371; Poggendorff's *Annalen*, cvii. p. 214.

PROCEEDINGS OF SOCIETIES.

Royal Society.

Researches on the Phosphorus-Bases.—No. VI. Phosphammonium-Compounds. By A. W. Hofmann, LL.D., F.R.S. &c.

[Received June 1, 1859.]

In several previous communications I have shown that dibromide of ethylene is capable of fixing either one or two molecules of tri-

ethylphosphine, a monatomic and a diatomic bromide being formed, which I have respectively represented by the formulæ—

Monatomic bromide.

$$C_{16}H_{19}PBr_2 = (C_4H_4)''Br_2 + (C_4H_5)_3P = \left[\begin{matrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ (C_4H_4Br) \end{matrix}\right\}P\left.\right]Br$$

and

Diatomic bromide.

$$C_{28}H_{34}P_2Br_2 = (C_4H_4)''Br_2 + 2\,((C_4H_5)_3P) = \left[\begin{matrix} (C_4H_5)_2 \\ (C_4H_5)_2 \\ (C_4H_5)_2 \\ (C_4H_4)'' \end{matrix}\right\}P_2\left.\right]''Br_2$$

There are other products formed, resulting from secondary reactions.

It was not quite easy to obtain a sufficiently satisfactory experimental foundation for the diatomic nature of the second compound. This substance presents an extraordinary degree of stability; in its general characters it is closely allied to the numerous monatomic bromides, both of the nitrogen- and of the phosphorus-series, which in the course of these researches have come under my consideration. Lastly, the oxygenated derivative of the bromide resembles so perfectly the monammonium- and the monophosphonium-bases, that more than once during my experiments I was inclined to doubt the correctness of my interpretation.

There is no direct proof of the diatomic character of the compound. Why should we reject the simple formula deducible from experiment? The hydrocarbons $C_n H_n$ are very prone to molecular transformations without change of composition. The idea suggested itself, that the diatomic saline molecule might be split into two monatomic saline molecules,

$$[(C_4H_5)_6(C_4H_4)''P_2]''Br_2 = 2\big([(C_4H_5)_3(C_2H_2)'P]Br\big).$$

It is true C_2H_2 figures in this formula as monatomic, whilst we should expect it endowed with diatomic substitution-power. But the connexion between composition and substitution-power is by no means finally settled; in fact, we know of many cases in which, under conditions not sufficiently established, the atomicity of a molecule changes: witness the radical "allyle," which is capable of replacing one or three equivalents of hydrogen.

But without going this length, the scission of diatomic ethylene into two monatomic molecules may take place in many other ways. The transformation of dibromide of ethylene into hydrobromic acid and bromide of vinyle,

$$(C_4H_4)''Br_2 = HBr + (C_4H_3)Br,$$

is a familiar example. The splitting of the ethylene-compound into bromide of formyle and bromide of methyle,

$$(C_4H_4)''Br_2 = (C_2H)Br + (C_2H_3)Br,$$

has never been observed, but did not appear altogether unlikely.

Our analytical methods are insufficient to distinguish between

$$[(C_4H_5)_3(C_2H_2)P]Br \text{ and } [(C_4H_5)_3(C_2H)P]Br;$$

and what I have represented as a diatomic ethylene-compound might have been, after all, a monatomic bromide—the bromide of formyl-triethylphosphonium, the complementary methyle-compound

$$[(C_4H_5)_3(C_2H_3)P]Br$$

existing possibly among the secondary products of decomposition.

In the presence of these and several similar self-raised objections, by which every observer endeavours to test the truth of his conclusions, I was induced again to appeal to experiment.

The prosecution of this line of the inquiry has led me to the discovery of a new class of diatomic bodies, which, while it confirms incontestably the correctness of my interpretation, appears to claim the attention of chemists for several other reasons.

I have established, in the first place, that the monatomic bromide

$$[(C_4H_5)_3(C_4H_4Br)P]Br$$

may be readily converted into the diatomic bromide

$$[(C_4H_5)_3(C_4H_4)''P_2]''Br_2$$

by the simple addition of triethylphosphine. Nothing is easier than to prove the transformation, the platinum-salt of the two bases presenting a remarkable difference of solubility, and other differences not less striking.

To remove every doubt, the bromide, obtained by treatment of the brominated bromide with triethylphosphine, was converted into the corresponding iodide, which in its properties and composition was found to be identical in every respect with the characteristic iodide, which I have fully described in my last note upon this subject.

The transformation of the monatomic into what I have represented as the diatomic compound being satisfactorily established, the conclusive experimental demonstration of the diatomic nature of the latter presented itself without difficulty in the conception of bromides containing at once phosphorus and nitrogen, the molecular expression of which would no longer admit of division.

This class of dibromides actually exists; they are readily produced by submitting the bromide of the brominated body to the action of ammonia or monamines instead of triethylphosphine.

I have formed as yet only three representatives of this new class of bodies, which I propose to designate as phosphammonium-compounds; their examination is sufficient to fix the character of the class; it would have been easy to construct scores of similar bodies.

Action of Ammonia upon the bromide of the brominated body.

The two substances, especially when in alcoholic solution, unite with evolution of heat—

$$[(C_4H_5)_3(C_4H_4Br)P]Br + H_3N = \left[\begin{matrix}(C_4H_5)_3\\(C_4H_4)''\\H_3\end{matrix}\begin{matrix}\}P\\\\\}N\end{matrix}\right]''Br_2.$$

Both the bromide and the corresponding chloride are very soluble, and little adapted for analysis; I have therefore fixed the nature of this body by the preparation and analysis of the platinum-compound. For this purpose the bromide generated in the above reaction was treated with oxide of silver; it is thus converted into a powerfully alkaline solution obviously of the dioxide,

$$\left[\begin{matrix}(C_4H_5)_3\\(C_4H_4)''\\H_3\end{matrix}\right\}\begin{matrix}P\\N\\H_2\end{matrix}\Big]''\Big\}O_4,$$

which, saturated with hydrochloric acid and mixed with dichloride of platinum, furnished a light-yellow crystalline platinum-salt, recrystallizable from boiling-water, and containing

$$[(C_4H_5)_3\,H_3\,(C_4H_4)''\,PN]''\,Cl_2,\,2PtCl_2.$$

Action of Ethylamine and Trimethylamine upon the bromide of the brominated body.

The phenomena observed with ethylamine and trimethylamine are perfectly analogous. These substances furnish, with the brominated bromide, new and very soluble dibromides, containing respectively

$$\left[\begin{matrix}(C_4H_5)_3\\(C_4H_4)''\\(C_4H_3)\,H_2\end{matrix}\right\}\begin{matrix}P\\N\end{matrix}\Big]''Br_2 \text{ and } \left[\begin{matrix}(C_4H_5)_3\\(C_4H_4)''\\(C_2H_3)_3\end{matrix}\right\}\begin{matrix}P\\N\end{matrix}\Big]''Br_2,$$

which, by treatment with oxide of silver, are converted into the corresponding powerfully alkaline oxides

$$\left[\begin{matrix}(C_4H_5)_3\\(C_4H_4)''\\(C_4H_5)\,H_2\end{matrix}\right\}\begin{matrix}P\\N\\H_2\end{matrix}\Big]''\Big\}O_4 \text{ and } \left[\begin{matrix}(C_4H_5)_3\\(C_4H_4)''\\(C_2H_3)_2\end{matrix}\right\}\begin{matrix}P\\N\\H_2\end{matrix}\Big]''\Big\}O_4,$$

and yield, by saturation with hydrochloric acid and precipitation with dichloride of platinum, two splendid platinum-salts crystallizing in long golden-yellow needles, and containing respectively

$$[(C_4H_5)_4\,(C_4H_4)''\,H_2\,PN]''\,Cl_2,\,2Pt\,Cl_2, \text{ and}$$
$$[(C_4H_5)_3\,(C_2H_3)_3\,(C_4H_4)''\,PN]''\,Cl_2,\,2Pt\,Cl_2.$$

By the formation of the phosphammonium-compounds, the nature both of the diammonium- and of the diphosphonium-series appears to me finally established.

It will be interesting to ascertain whether the brominated bromide, when submitted to the action of monarsines and monostibines, will give rise to the formation of phospharsonium- and phospho-stibonium-bases. The solution of this question will not be difficult.

THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Observations on Chromium. By Professor WÖHLER.

Metallic Chromium.—Chromium may be easily reduced from the violet chloride by fusing zinc. The following is the process:—

1 part of perchloride of chromium is mixed with 2 parts of chloride of potassium and sodium (composed of 7 parts $NaCl^2$ and 9 parts KCl^2), the mixture is pressed firmly into a common crucible, 2 parts of granulated zinc are laid upon it, and this is again covered with a layer of the above flux. The crucible is then gradually heated until the mass becomes red-hot and fuses. As soon as a bubbling noise, caused by the boiling of the zinc, is heard, and a zinc flame is observed on the momentary removal of the cover of the crucible, the heat is diminished by closing the draught, and the mass is kept in a fluid state for about ten minutes. The crucible is then taken out, gently shaken to facilitate the accumulation of the metal, and left to cool. Permitting it to cool slowly with the furnace, appears to have no influence upon the crystallization of the chromium.

On breaking up the crucible, a well-fused regulus of zinc is found beneath a green slag. When it has been well washed in water, its surface usually glitters with small crystals of chromium. It is laid in dilute nitric acid, which is renewed until all the zinc is dissolved. The chromium remains as a grey crystalline powder, which, in order to make sure that all the lead which is contained in common zinc has been removed, is heated once more with nitric acid, and then well washed.

The quantity of chromium obtained from 30 grms. of chloride was in one instance 6 and in another 7 grms. According to calculation 10 grms. ought to be obtained. The loss may depend partly upon the unavoidable partial oxidation of the perchloride of chromium by access of air, as indicated by the green colour of the slag, and partly upon the fact that a small portion of the chromium appears to enter into actual combination with the zinc, and to be dissolved with the latter by the acid, as is indicated by the bluish-green colour of the solution of zinc.

The chromium thus prepared is a pale-grey, crystalline powder. Even with a magnifying power of 50 diameters crystalline aggregates of a pine-tree like form are detected in it, together with very acute single rhombohedra of great lustre and nearly of a tin-white colour. When the reduction is effected on a large scale, the crystals will certainly be obtained of a size which will enable their form to be determined with accuracy. The spec. grav. was found =6·81 at 68° F.; 4·742 grms. were employed in this determination.

When heated to redness in the air, it acquires yellow and blue tints, like steel, but without burning. By degrees it becomes covered with a thin coat of green oxide, but even 0·5 grm. could not be completely oxidized by ignition for an hour in the air. When sprinkled into the flame of a spirit-lamp fed with oxygen gas, it burns with scintillations, but less brilliantly than iron. On the other hand, it burns upon chlorate of potash when this is scarcely heated to fusion, producing a dazzling white fire and forming chromate of potash. It is oxidized very readily, but without incandescence, by fusing nitrate of potash. In fusing carbonate of soda it remains unaltered.

Muriatic acid dissolves it with ease, evolving hydrogen gas, and forming blue protochloride. Dilute sulphuric acid, which readily dissolves iron, has no action upon it; but on the application of a gentle heat, a very violent action suddenly takes place; and if the residue of the metal be washed, it is found to have acquired the property of being soluble in even the most dilute sulphuric acid without the aid of heat. It is not acted upon in the least even by boiling concentrated nitric acid.

When heated in chlorine gas, it smoulders away quickly to form violet perchloride.

When placed in a platinum tray in a tube of Bohemian glass and kept at a strong red heat for an hour in a current of aqueous vapour free from air, carried up from hot water by carbonic acid gas, it was found only to have acquired a superficial coat of green oxide.

This chromium might possibly be a compound of zinc. 0·5 grm. was therefore dissolved in muriatic acid with the addition of a little nitric acid, and the oxide of chromium thrown down by carbonate of baryta. No trace of zinc could be detected in the filtrate.

In an attempt to reduce chromium from its perchloride in the above way by means of cadmium, in the hope that perhaps better crystals might be thus obtained, the mass exploded as soon as its fusion took place, with such violence that nothing was left in the crucible. The cause of this was either the far more violent instantaneous action of the cadmium, or its sudden conversion into vapour. With magnesium, on the contrary, the reduction took place, but there is no advantage in employing that metal rather than zinc.

The preparation of large quantities of perchloride of chromium is attended with numerous difficulties. This beautiful substance may, however, be readily prepared in any quantity in the following way. The mixture of oxide of chromium and charcoal is made into small balls with starch-paste; these are calcined in a covered crucible,

and then put into a crucible the bottom of which is furnished with an opening, into which about 6 inches of a narrow porcelain tube is luted. The orifice of this tube, which projects but little above the bottom of the crucible, is furnished with a small cover, to prevent the balls from falling through. The crucible is covered with a smaller one, reversed and luted to the opening; the bottom of this is also perforated with a small hole, for the escape of the carbonic oxide gas. This apparatus is placed upon the grating of an ordinary furnace in such a way that the porcelain tube passes through beneath the grating, where it may be united with the conducting tube of an apparatus for the evolution of chlorine. After the apparatus has been filled with dry chlorine, the lower crucible is brought to a strong red heat, and the fire is regulated so that the chloride produced may condense in the form of a sublimate in the upper crucible, which at the utmost only attains slight redness. As perchloride of chromium is converted into peroxide when heated in contact with the air, it is of importance to continue the passage of chlorine through the apparatus until it has become cold. As a matter of course the operation must be performed in the open air, or under a chimney with a strong draught. The chloride must afterwards be washed with water, because it contains chloride of aluminium derived from the crucible. If care be not taken that the current of chlorine is strong enough, some protochloride is formed, and during the treatment with water this causes the solution of much perchloride, which is thus lost.

Magnetic Oxide of Chromium.—In preparing crystallized oxide of chromium by the author's process, by heating the vapours of the oxychloride, Neger remarked, in using accidentally a magnetic knife for separating the crusts of oxide from the glass, that some portions of this oxide were strongly magnetic, a circumstance which appeared sufficiently remarkable to call for further investigation. That it could not be due to the accidental presence of iron, was at once clear from the nature of the materials employed in the preparation of the oxychloride. Nevertheless, for the sake of certainty, about 1 grm. of the magnetic oxide was converted into chromic acid by fusion with nitrate of potash and carbonate of soda, but no trace of iron could be detected.

It was therefore very probable that the magnetic oxide was a protoperoxide of chromium analogous to the magnetic ironstone. Similar compounds have actually been already obtained from protochloride of chromium by Bunsen with the electrical current, and by Peligot in the form of a very alterable hydrate. But no one mentions the magnetic properties of this body.

The first thing to be ascertained was whether the magnetic oxide is produced from the oxychloride at a very high or at a moderate temperature. When the decomposition of the vapour was effected in a porcelain tube at a white heat, the oxide obtained was quite unmagnetic and beautifully crystallized. The decomposition was therefore effected in a glass tube, which was surrounded with red-hot coals, but not heated to redness. In this way it was found that

the decomposition of the oxychloride takes place far below a red heat, and that the oxide thus formed is strongly attracted by the magnet; only a few fragments, which had probably been too strongly heated, did not follow it.

The magnetic oxide forms uncrystalline, black crusts, which are readily separable from the glass, dull on the inner surface, shining on the surface applied to the glass, and in their fracture exactly resembling iron scale. When pounded, it furnishes a black powder, and when laid in a thin coat upon glass it is translucent and brown; whilst the crystallized, unmagnetic oxide furnishes a green powder, and transmits a green light when in thin layers. It is strongly attracted by the magnet, and in crusts even exhibits a slight polarity. When heated to redness in contact with the air it becomes greenish, and loses the magnetic property, without any glow. When heated in dry chlorine gas, free from air, it furnishes a little oxychloride and also becomes unmagnetic.

If this oxide be $CrO + Cr^2O^3$, 100 parts, when ignited in contact with air, should give 103·5 parts of peroxide of chromium, and therefore increase in weight by 3·5 parts. Experiments, however, showed immediately that, on the contrary, it loses about as much or more in weight. In one experiment it lost 5·4 per cent. in weight. But this oxide contained a small quantity of chromic acid, extractible by water. Another portion was therefore pounded, treated with ammonia, and washed. 1·357 grm. of this oxide was put into a glass bulb, and heated over the large spirit-lamp in a current of well-dried hydrogen gas, free from air. When the heat approached redness, the mass began to glow, and the formation of water commenced. After this had quite ceased, and the oxide had cooled in the current of gas, it weighed 1·308. It had therefore lost 3·5 per cent. of oxygen. When subsequently heated in the air, it did not change its weight. The water produced exhibited no trace of acid reaction.

From this it follows that the magnetic oxide cannot be pure protoperoxide; but from its magnetic property we may conclude with great probability that it contains that compound as an essential constituent, mixed or combined with a higher oxide. This higher oxide is probably the blackish-brown binoxide of chromium, CrO^2, which may also be regarded as chromate of chromium. If we suppose that the magnetic oxide is a compound of $(CrO + Cr^2O^3) + 3CrO^2$, it would necessarily lose 1 atom of oxygen, or 3·33 per cent. in weight when heated to redness, which nearly agrees with the experiment in hydrogen gas. Nevertheless it is a more probable supposition that it only contains the brown oxide intermixed, and indeed in variable quantities according to the temperature at which it was produced. It will also most probably contain intermixed free oxide, Cr^2O^3, formed at those places in the tube where the heat was too high. An attempt to obtain it pure by passing the vapour of oxychloride of chromium through a glass tube heated to about 572° F. in the oil-bath, proved that no decomposition takes place at that temperature. Many other experiments made with the view of preparing the magnetic oxide from the oxychloride in other ways, did

not answer expectation. Nor was it produced when, as above mentioned, metallic chromium was ignited in aqueous vapour.

As the metal in the magnetic protoperoxide of iron is the most magnetic of all metals, we might conclude from this that the metal in the magnetic oxide of chromium also belongs to the stronger magnetic bodies. But this is not the case; metallic chromium, taken in the ordinary sense, and tested in the ordinary way, is not magnetic, and does not divert the magnetic needle in the least, no matter whether it be prepared from the perchloride by zinc, or in the blast-furnace from the oxide by charcoal, or by the electrical current from chromic acid or perchloride of chromium. When the smallest quantity of iron was contained in the solution of the latter, however, the reduced chromium acquired the property of diverting magnetic needles. In fact, it deserves notice that neither peroxide nor protoxide of iron is magnetic by itself, but that these oxides acquire the magnetic property of the metal contained in them as soon as they combine with each other in equivalent propertions. This must appear still more remarkable in the case of chromium, as that metal is not itself magnetic.—*Nachrichten von der Königl. Ges. der Wissensch. zu Göttingen*, 1859, p. 147.

On Solanine. *By* Otto Gmelin.

The author was engaged in an investigation of solanine in Redtenbacher's laboratory last year. Liebig obtained information of this from Redtenbacher as early as the 2nd of June, 1858, and states at the beginning of the present memoir that at that date the author had found that solanine is a glucoside, and free from nitrogen. Zwenger and Kindt likewise discovered early in the present year* that solanine may be decomposed by acids into grape-sugar and a base to which they give the name of solanidine.

The author now furnishes a long series of analytical data, from which it appears that both solanine and solanidine are free from nitrogen. The analyses lead to the following numbers:—

1. *Analyses of Solanine*:—

	Grm.		CO^2 and HO		In 100 parts. C and H	
(1)	0·3711	gave	0·8442	0·2913	62·04	8·74
(2)	0·3637	„	0·8242	0·2864	61·80	8·75
(3)	0·3506	„	0·7973	0·2745	62·02	8·75
(4)	0·4041	„	0·9221	0·3208	62·23	8·84
(5)	0·3686	„	0·8409	0·2893	62·22	8·72
(6)	0·3816	„	0·8644	..	61·78	..
(7)	0·4402	„	1·0143	0·3453	62·84	8·69
(8)	0·3707	„	0·8525	0·2903	62·72	8·70
(9)	0·4198	„	..	0·3272	..	8·66
(10)	0·4499	„	1·0193	0·3494	61·81	8·63
(11)	0·4052	„	0·9272	0·3188	62·41	8·74

On boiling solanine with dilute sulphuric acid, the author obtained

* Page 308 of the present volume.

from 100 parts of solanine in three experiments:—

(1) 65·4 grape-sugar,
(2) 65·1 „ „
(3) 65·3 „ „

2. The *analyses of solanidine*, the second product of decomposition obtained by boiling solanine with acids, gave:—

	Dried over sulphuric acid.		Dried at 212° F.	
Carbon	82·04	81·96	83·96	85·10
Hydrogen	10·84	10·58	10·75	10·89

Analyses of muriate of solanidine gave for 100 parts:—

		In 100 parts C	H	Cl
(1) 0·3938 gave 1·0654 CO^2 and 0·3594 HO;		73·78	10·14	..
(2) 0·4000 „ 1·0833 „ „ 0·3678 „		73·86	10·22	..
(3) 0·3226 „ 0·1111 AgCl		..	..	8·52
(4) 0·2683 „ 0·0901 „		..	..	8·31
(5) 0·3863 „ 0·1358 „		..	..	8·70

The analysis of a portion subsequently obtained in the same way, which also crystallized in colourless needles and appeared homogeneous under the microscope, furnished a result differing considerably in the amount of carbon.

0·2970 grm. gave 0·7836 CO^2 and 0·2785 HO, consequently in 100 parts, 71·96 C and 10·42 H.

The author states expressly that he was unable to overcome the difficulties of purifying both solanine and solanidine sufficiently to enable him to establish the composition of these bodies with certainty. They may, however, be approximately expressed by the following formulæ:—

Solanine. Solanidine.
$$C^{88}H^{72}O^{30} - 3C^{12}H^{12}O^{12} + 6HO + 4O = C^{52}H^{42}O^{4};$$

Solanidine.
$$C^{52}H^{42}O^{4} - 2HO = C^{52}H^{40}O^{2};$$

Solanidine.
$$C^{52}H^{42}O^{4} + ClH = C^{52}H^{43}ClO^{4};$$

Solanine.	In 100 parts.			Solanidine.			
C	62·19	88=528	62·86	C	82·00	52=312	80·83
H	8·72	72	72 8·57	H	10·71	42	42 10·88
O	29·09	30	240 28·57	O	7·29	4	32 8·29

Equivalent weight calculated 280=840:3, found average 278.

Solanidine −2HO.				Perchloride of solanidine.			
C	85·10	52=312	84·78	C	73·82	52=312	73·85
H	10·89	40	40 10·87	H	10·18	43	43 10·18
O	4·01	2	16 4·35	Cl	8·51	1	35·5 8·40
				O	7·49	4	32 7·57

The solanine was prepared in the ordinary way described by Otto. By solution in muriatic acid, precipitation with ammonia, and frequent recrystallization from nearly absolute alcohol, the author at last obtained solanine in beautiful, colourless, silky needles of considerable length, in which nothing heterogeneous could be detected by the microscope.

The author prepared his solanidine by boiling solanine with dilute sulphuric acid. When heated only to about 122° F. with a dilute mineral acid, the solanine is decomposed into the compound of solanidine with the acid, which is difficult of solution in an excess of acid, and grape-sugar, which may be easily detected by all its characteristic reactions. If ammonia be added to the acid fluid, the turbidity first of all disappears; a further addition precipitates the solanidine almost entirely in crystalline flakes. If the precipitate be separated by filtration and recrystallized at once from alcohol, it dissolves, even when boiled, very slowly and imperfectly; but if the body be once dissolved, or the precipitate be first of all dried in the air, it becomes readily soluble in alcohol. The body, when repeatedly crystallized from alcohol, forms colourless, indistinctly crystalline crusts. It is volatile in a current of carbonic acid, but becomes slightly brown.

The author also attempted, like Moitessier, to æthylize solanine, and boiled a large quantity of pure solanine, sealed up in a tube with an excess of iodide of æthyle, at a temperature of about 234° F. on the salt-bath, with a perfectly negative result. After the excess of iodide of æthyle was distilled off, the resinous mass was dissolved in boiling water, precipitated by ammonia, and recrystallized from alcohol. Both under the microscope and when analysed, it proved to be unaltered solanine.—Liebig's *Annalen*, cx. p. 167.

On Alcoholic Fermentation. *By* L. Pasteur.

When the accurate analyses of Gay-Lussac and Thenard and those of De Saussure had definitely established the composition of sugar and alcohol, it became easy to show theoretically that by mixing alcohol and carbonic acid, the composition of sugar might be reproduced. This was indicated by Gay-Lussac in a letter addressed by him to M. Clement in 1815, which concludes thus:—"If we suppose now that the products furnished by the ferment may be disregarded in relation to the alcohol and carbonic acid which are the only sensible results of fermentation, we shall find that of 100 parts of sugar, 51·34 are converted into alcohol, and 48·66 into carbonic acid during fermentation." This deduction of Gay-Lussac coincided with the views promulgated twenty-five years before by Lavoisier upon alcoholic fermentation, and it removed all the doubts which sooner or later must have been raised by the inaccurate experiments of that illustrious chemist.

It was admitted, however, that experiment could not in all points confirm Gay-Lussac's theories, for Lavoisier had rightly indicated that a small portion of sugar was transformed into an organic acid,

which he supposed to be acetic acid, but which has long since been identified with lactic acid.

The results of the author's experiments are at variance with the general opinions upon the products of fermentation:—

1. The acid of alcoholic fermentation is never either acetic or lactic acid.

2. Alcohol and carbonic acid are not the only products of the splitting-up of sugar. They are always accompanied by succinic acid and glycerine. The proportion of succinic acid varies between 5 and 7 thousandths, and that of glycerine between 25 and 36 thousandths of the weight of sugar set in fermentation.

3. The alcohol and carbonic acid do not equate with a definite weight of sugar, that is to say, the alcohol and carbonic acid are not in the proportions indicated by the theoretical equation; more carbonic acid is evolved than is required by the weight of alcohol produced.

4. More than 1 per cent. (1·2 to 1·5) of the weight of sugar is fixed upon the yeast in the form of various matters, amongst which are cellulose and fatty substances.

Thus of 100 grms. of sugar which are fermented, 5 to 6 grms. do not follow the equation of Lavoisier and Gay-Lussac; and this portion of sugar is transformed by assimilating water in such a way as to furnish in ordinary cases—

	grm.	grm.
Succinic acid	0·6 to	0·7
Glycerine	3·2 „	3·6
Carbonic acid	0·6 „	0·7
Cellulose, fatty matters, and other products still undetermined	1·2 „	1·5
Total	5·6 to	6·5

The remainder of the sugar appears to correspond with the whole of the alcohol and the rest of the carbonic acid, in accordance with the equations of Lavoisier and Gay-Lussac.

The question here arises whether the succinic acid and glycerine with the carbonic acid which accompanies them, may not be the results of a secondary and accidental action. This the author cannot admit, as in more than a hundred analyses of fermentations effected under the most different conditions, these products were always obtained.

In wine also he found that succinic acid and glycerine are present in considerable quantity; 1 litre of wine contains 6 to 8 grms. of glycerine, and 1 to 1·5 grm. of succinic acid. The solid residue of the evaporation of a litre of wine being from 15 to 25 grms., it will be seen that more than a third, and often more than half of the solid materials of wine have been unknown to the present day.—*Comptes Rendus*, June 27, 1859, p. 1149.

On some Products of the dry Distillation of Acetates.

By Dr. R. Fittig.

Amongst the products of dry distillation, the aldehyde and acetone of the acid have long since been recognized. Limpricht showed that amongst the products of the dry distillation of butyrate of lime the compounds $C^{16}H^{16}O^2$ and $C^{32}H^{32}O^2$ occur, and Friedel subsequently discovered the compounds $C^{10}H^{10}O^2$ and $C^{12}H^{12}O^2$ among the same products.

According to the author's statements, the acetates behave in the same way as the butyrates. By their dry distillation he obtained two compounds, $C^6H^6O^2$ and $C^{10}H^{10}O^2$, homologous with acetone, also the compound $C^{12}H^{10}O^2$, known as dumasine and other products.

Crude acetone and the brown fluid which floats upon crude acetone were submitted to fractional distillation. The author first collected the portion boiling between 140° and 266° F., and then decomposed this into three compounds by about thirty rectifications. These were—

$C^6H^8O^2$; boiling-point 167°—170°·6 F.
$C^{10}H^{10}O^2$; „ „ 194°—203° F.
$C^{12}H^{10}O^2$; „ „ 248°—257° F.

1. $C^6H^8O^2$ (*Methylacetone*).—A colourless fluid, smelling like acetone, miscible with water and alcohol in all proportions, boiling between 167° and 170°·6 F., and having a spec. grav. of 0·838 at 66° F. Analysis:—

C	66·0	8 =	48	66·6
H	11·2	8	8	11·1
O	..	2	16	22·3

The compound mixes with bisulphite of soda with a strong evolution of heat, and in course of time the fluid solidifies by separation of crystals, the composition of which is $C^6H^7NaS^2O^6+3HO$. They are readily soluble in water, and cannot be recrystallized therefrom.

2. $C^{10}H^{10}O^2$ (*Æthylacetone*).—A limpid fluid, with a slight odour of acetone, which dissolves with difficulty in water, but mixes with alcohol in all proportions, boils between 194° and 203° F., and has a spec. grav. of 0·842 at 66° F. Analysis:—

	I.	II.		
C	70·4	69·5	10 = 60	69·8
H	11·2	11·3	10 10	11·6
O	..	..	2 16	18·6

This compound mixes with bisulphite of soda with strong evolution of heat, and in course of time the mixture solidifies with separation of colourless, pearly laminæ, which are readily soluble in water. Their composition is $C^{10}H^9NaS^2O^6+3HO$.

3. $C^{12}H^{10}O^2$ (*Dumasine*).—A colourless oil, which becomes yellow by long standing, and has a peculiar, but not unpleasant

odour. It is lighter than water, and insoluble in that fluid, but dissolves in alcohol in all proportions; its boiling-point is between 248° and 257° F. Analysis:—

	I.	II.		
C	73·7	74·3	12=72	73·5
H	11·1	11·0	10 10	10·2
O	..	..	2 16	16·3

Kane ascribes the formula $C^{10}H^8O$ to the body which he calls dumasine. The preceding analyses lead to the same formula which Heintz afterwards proposed for this body.

If dumasine be brought in contact with a concentrated solution of bisulphite of soda, neither mixture nor evolution of heat takes place at first, but by continued agitation or long standing the oil floating on the surface solidifies completely into a crystalline mass, which in external appearance resembles the other compounds of this kind. It is readily soluble in water; boiling water decomposes it immediately with deposition of dumasine.

The analyses which the author made of this compound did not agree very well together; nevertheless they appear to lead to the formula $C^{12}H^9NaS^2O^6+6HO$.

Dumasine is converted into oxalic acid by concentrated nitric acid; dilute nitric acid has no action upon it.

By the distillation of dumasine with muriatic acid and brown oxide of manganese, a colourless oil is obtained, which is heavier than water, boils between 302° and 311° F., and does not combine with alkaline bisulphites. Its analysis gave—

C	43·2	12=72	43·1
H	5·4	8 8	4·8
Cl	41·7	2 71	42·5
O	..	2 16	9·6

Liebig's *Annalen*, cx. p. 17.

On the Combinations of the Polyatomic Alcohols with the Bibasic Acids. *By* M. Desplats.

The researches of Berthelot upon the combinations of glycerine and saccharine matters with the monobasic acids, have established the general relations which preside over the mutual combination of the monobasic acids and polyatomic alcohols, but the action of the bibasic acids upon these alcohols is still very little known.

The author took for his starting-point in his researches a well-marked bibasic acid, tartaric acid, and a triatomic alcohol, glycerine. Between these two bodies we may assume:—

1. An acid compound formed by 1 equiv. of tartaric acid and 1 equiv. of glycerine, with elimination of 2 equivs. of water, a compound corresponding with the sulphoglyceric acid of Pelouze;

2. An acid compound formed by the union of 2 equivs. of tartaric acid and 1 equiv. of glycerine with elimination of 4 equivs. of water;

3. An acid compound formed by 3 equivs. of tartaric acid and 1 equiv. of glycerine with elimination of 6 equivs. of water.

Moreover, each of these three categories may include several other acid compounds, according as the glycerine loses more or less water in combining with the tartaric acid. The following are the results at which the author has arrived:—

I. *Glycerimonotartaric Acid.*

$C^{14} H^{12} O^{16} = C^8 H^6 O^{12} + C^6 H^8 O^6 - 2HO$, monobasic.

This compound is obtained by heating equal parts of tartaric acid and glycerine to 212° F. for forty hours. The author analysed the lime-salt, $C^{14} H^{11} CaO^{16}$ (which had already been obtained by Berzelius), and also the baryta-salt, $C^{14} H^{11} BaO^{16}$. He prepared the salts of magnesia, lead, copper, zinc, and silver. All these salts are soluble in water, and undergo a slow decomposition therein; the glycerine fixes the elements of water again, and the acid is regenerated. This decomposition is accelerated by the action of baryta- or lime-water.

II. *Glyceriditartaric Acid.*

$C^{22} H^{16} O^{26} = 2(C^8 H^6 O^{12}) + C^6 H^8 O^6 - 4HO$, bibasic.

This compound is obtained by heating equal parts of tartaric acid and glycerine, in presence of a certain quantity of water, to 212° F. for fifty hours. The author analysed the lime-salt, $C^{22} H^{14} Ca^2 O^{26}$, and the salt of baryta, $C^{22} H^{14} Ba^2 O^{26}$.

III. *Epiglyceriditartaric Acid.*

$C^{22} H^{14} O^{21} = 2(C^8 H^6 O^{12}) + C^6 H^8 O^6 - 6HO$, monobasic.

This acid differs from the preceding only in containing 2 equivs. less water, and in a corresponding diminution in its basicity; it corresponds with Berthelot's epidichlorhydrine. It is obtained by heating equal parts of glycerine and tartaric acid for a great many hours to 284° F.

The analysis of lime-salt gave $C^{22} H^{13} CaO^{24}$, and that of the baryta-salt, $C^{22} H^{13} BaO^{24}$.

IV. *Glyceritritartaric Acid.*

$C^{30} H^{22} O^{38} = 3C^8 H^6 O^{12} + C^6 H^8 O^6 - 4HO$, quadribasic.

In the formation of this compound the amount of water eliminated is less than the normal 6 equivs., and a corresponding portion of the basicity of the tartaric acid is preserved. It is obtained by heating glyceriditartaric acid with fifteen times its weight of tartaric acid, or 1 part of glycerine with 20 parts of acid, and keeping the temperature at 284° F. for thirty hours.

The lime-salt corresponds with the formula $C^{30} H^{18} Ca^4 O^{38}$, and the formula of the baryta-salt, $C^{30} H^{18} Ba^4 O^{38}$. These formulæ were checked by saponifications.—*Comptes Rendus*, August 1, 1859, p. 216.

ANALYTICAL CHEMISTRY.

Volumetric Determination of Mercury. *By* C. W. Hempel.

In this method it is necessary, in the first place, that the mercury in a solution in which it is to be determined, shall be converted into protochloride. This is then dissolved in the process, by iodine and iodide of potassium. If protochloride of mercury mixed with muriatic acid be agitated with a considerable excess of solution of iodine, all the protochloride is soon converted into scarlet periodide of mercury, which entirely disappears on the addition of a sufficient quantity of iodide of potassium.

If the muriatic acid be entirely left out, and the protochloride of mercury mixed with an excess of a solution of 1 equiv. of iodine and 3 equivs. of iodide of potassium, the protiodide of mercury first produced becomes completely converted into periodide immediately on its being shaken, but this now remains in solution:—

$$Hg^2Cl + 3KI + I = 2(HgI + KI) + KCl.$$

1·178 grm. of protochloride of mercury and 2·5 grms. KI were put into a stoppered bottle, and 100 cubic centims. of a solution of $\frac{1}{10}$th of iodine in KI (equivalent weight of the iodine = 127) were added. The bottle was quickly stopped and then shaken until there was no longer any precipitate, for which purpose a few moments sufficed. A solution of $\frac{1}{10}$th of hyposulphite of soda (24·8 grms. in the litre) was then poured into the brownish-red fluid until all colour had disappeared, and the fluid had become limpid; for this purpose 50·8 cub. centims were required. The whole was then diluted with water to 500 cubic centims.

50 cubic centims. were then taken out by the pipette, and after the addition of filtered starch-paste, mixed with the normal solution of iodine until the appearance of a bluish colour.

In six experiments 0·09 cubic centim. were employed each time to 50 cubic centims., or in all 10·09 cubic centims. of solution of iodine. Deducting from this the quantity of solution of iodine which corresponds with the equivalent solution of hyposulphite of soda added to each 50 cubic centims. (namely 5·08 cubic centims.), there still remain 5·01 cubic centims. of solution of iodine. This quantity represents 0·11798 grm. of protochloride of mercury instead of 0·1178 grm.

There is consequently no doubt that protochloride of mercury may be very accurately determined by means of iodine.—Liebig's *Annalen*, cx. p. 176.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On proposed Improvements in the Manufacture of Kelp. *By* William Wallace, Ph.D., F.C.S., *Glasgow**.

The kelp manufacture is not less important to the iodine maker, the alum maker or the physician, than it is to the poor peasant of the

* Communicated by the Author; having been read before the British Association Meeting at Aberdeen, September 14, 1859.

Western Islands, who toils hard in its preparation, and receives but sorry remuneration for his services. The present mode of fabrication possesses many disadvantages; and the object of this communication is to point out means by which, it is anticipated, these may be in some degree removed, and a superior article manufactured which would command a much higher price, and perhaps enable the peasantry of the Hebrides to live more comfortably than they are able to do at the present time. Mr. Donald M'Crummen, who is well known, I believe, to many of the proprietors of the Highland kelp shores, is the originator of the principal proposal contained in this notice; indeed a gold medal was awarded to him by the Highland Society in 1847 for a paper upon this subject. I have lately co-operated with Mr. M'Crummen in some experiments bearing on this subject; and it was at the solicitation of that gentleman that I agreed to make known our views at the meeting of the British Association at Aberdeen, with the hope that this exposition may lead to some amelioration in the social state of the islanders, or at least direct attention to the subject.

Kelp is obtained by burning dried sea-weed of various kinds in shallow pits. It is not my intention to describe the process in detail, as it is sufficiently well known to all those who are likely to be interested in this communication; but I may refer those who are not acquainted with the present mode of manufacture, to an excellent and highly interesting paper by Mr. Charles Glassford in the second volume of the Transactions of the Philosophical Society of Glasgow.

The chief disadvantages of the present system of working are:—

1. The desiccation of the weed being effected by the heat of the sun, the period during which kelp can be made is necessarily limited to the summer and autumn months, although it is well known that the plants richest in iodine, and therefore capable of producing the most valuable kelp, are cast ashore in greatest abundance during winter and spring, and are generally allowed to rot or be washed away. Again, there is constant danger of the weed, after it has been collected, being deteriorated or rendered altogether worthless by the setting in of rainy weather; for the kelp prepared from weed which has been exposed to rain for a few days is almost worthless, the potash-salts and iodine being readily washed out. To these considerations it may be added that during the winter months, when large drifts are thrown upon the shores, the male population of the islands have little or no employment.

2. As the bed of the pit upon which the weed is burned is simply the shingly or sandy beach or the bare soil, much sand, clay, and stones is almost unavoidably mixed up with the product, and this gives a kind of licence to the dishonest kelper to adulterate his product with stones and sand, sometimes to the extent of 50 per cent.

3. The very high temperature to which the burning weed is subjected, carbonaceous matter being present, causes the deoxidation of much of the alkaline sulphates, with the consequent formation of sulphides, sulphites, and hyposulphites. These compounds become concentrated in the residual mother-liquor, and cause an enormous

waste of sulphuric acid in their neutralization, while the offensive and poisonous gases evolved cause a serious nuisance in the neighbourhood. The cost of working kelp, that is, extracting from it its various constituents, is about 25*s.* to 28*s.* per ton, of which no less than 11*s.* to 13*s.*, or nearly a half, is for vitriol, the principal part of which is consumed in neutralizing the sulphides and decomposing other sulphur compounds formed in the burning process. The high temperature required to bring the salts into a fused state has also the effect, it appears, of expelling a portion of the iodine, and an appreciable quantity of the salts themselves.

Mr. M'Crummen has kindly prepared for me a quantity of the salts from different kinds of weeds. In each case a particular plant was treated, and the varieties were *Laminaria digitata*, or deep-sea tangle, *Fucus serratus*, or black wreck, sometimes called sea-oak, and *Fucus nodosus*, called by the kelpers yellow or bladder wreck. The first of these yields the best drift-weed kelp, while the other two furnish cutweed. Without going into the details of the analyses, it may be sufficient to give the quantities of potash and iodine, the only valuable ingredients in the salts, which, having been carefully prepared by charring at a rather low heat, were quite white, and almost entirely free from sulphides and other injurious sulphur compounds. The following Table represents the quantities of potash per cent., and of iodine per kelp ton in the pure salts, in the ashes of the plants, and in the two varieties of ordinary kelp:—

		Laminaria digitata.	*Fucus serratus.*	*Fucus nodosus.*
Pure salt ..	Potash....	34	31	23
	Iodine....	38	15	10
Ash	Potash....	26	19	14
	Iodine....	28	9	6
		Very fine drift.		Cutweed.
Kelp.....	Potash....	24		16½
	Iodine....	18		4

The great disparity observable in these results with regard to the iodine, cannot be accounted for entirely by the admixture in the kelp of various impurities; it must be owing in some degree to the actual volatilization of the iodide of sodium during the burning of the weed.

With regard to the suggestions for improving the process, I must premise that I state the views of Mr. M'Crummen and myself with great diffidence, and rather in the hope of exciting interest in, and attention to the subject, than in the expectation that our proposals will be carried out in practice. It is quite obvious that the kelpers could not undertake the separation of the kelp or charred sea-weed into its constituent salts, and the preparation of iodine from the mother-liquor. It is even doubtful whether they could undertake the solution of the kelp or burnt ash, and the evaporation of the lye; but if this could be effected, it would be a very great improvement. The treatment recommended in this case would be to burn

the weed carefully, so as to char the organic matter and convert the whole into a loose ash, lixiviate with a small quantity of water, and evaporate the solution to dryness. The ash could be treated with water several times, and the liquors added to the evaporating pan until they became rather weak, when they could be used, in place of water, to lixiviate a fresh quantity of ash or charred weed. By this treatment a very pure salt would be obtained, the iodine would be wholly preserved, while the cost of working would be more than counterbalanced by the saving of vitriol that would be effected by the absence of the sulphur compounds already referred to. The insoluble matter containing phosphate of lime, charcoal, &c., would be preserved to the peasants for manuring their ground.

The main objects desired to be attained, the preservation of the iodine, and the non-formation of sulphur compounds, would be accomplished by simply charring the weeds so as to produce a loose ash, without the necessity for subjecting it to any further treatment; but it is to be feared that this material would be objectionable from the difficulty of conveying it.

It is of the utmost importance that the proper weeds should be selected, and that these, when obtained, should be preserved from the action of rain, which soon destroys all descriptions of sea-weeds. The most valuable weed is the deep-sea tangle, or *Laminaria digitata*, called in some parts of the Highlands "Bardarrig," in others "Stamph," and in Ireland "Sea-rods." It consists of a very thick stem from 2 to 6 feet long, having at the end a frond divided into a variable number of branches or fingers. Well-made and unadulterated kelp from this weed, I have been informed by a gentleman thoroughly acquainted with the manufacture as well as the working of kelp, should contain from 15 to 20 pounds of iodine per ton. Next in quality is the shore-tangle, which can be cut at low water in spring-tides. This is the *Laminaria saccharina*, called by the kelpers "Slatenvarra." It consists of a stem from a few inches to 3 feet long, and never more than half an inch thick, terminated by a long, flat, undivided frond, from 1 to 6 or even 10 feet long, and 2 to 12 inches broad. This plant also makes tolerably good kelp; but the quantity of iodine in it is only about half that of the true drift-weed kelp. Pure drift kelp, made from bardarrig only, is highly porous, and not by any means so vitreous or saline in appearance as the inferior kinds; indeed it is generally supposed that the sea-rods cannot be burned alone in such a manner as to make a fused mass; and hence it is always more or less adulterated, sometimes to a large extent, with the ashes of the commonest weeds cut from the rocks. This inducement or necessity for sophistication would cease to exist if the product required was merely a loose ash.

Of the varieties of cutweed, it will be evident, from the remarks already made, that the black wreck is very much superior to the yellow or bladder wreck; and in addition to the superiority of the kelp or ash, I have found that the quantity of weed required to make a ton of the product is much greater for the latter than the former.

Another point of importance is that the islanders should be instructed to employ whatever means may be within their reach to store up during winter and spring a quantity of the best weed washed ashore during stormy weather. The Irish peasants are constantly in the habit of collecting these weeds, and, in the absence of better shelter, building them into stacks or quiles, which protect them from the rain. In the Hebrides, however, this source of first-class material appears to be generally neglected; but this is probably owing, in great part, to the colder and more humid climate of these islands. If the proprietors of kelp shores would erect, at the most favourable places, extensive drying sheds, a great quantity of the deep-sea tangle might be desiccated during the winter and spring, and burnt whenever favourable weather set in. These sheds would be useful during wet weather at all seasons of the year; for even the strongest tangles are completely destroyed by exposure to three or four days' rain, while the cutweeds are wasted away in a much shorter period. It is also important that suitable premises should be provided for storing the kelp or ash until it can be shipped; for much valuable material is greatly deteriorated by exposure to rain, insufficiently kept off by a loose covering of heather.

It would be productive of much benefit, if the proprietors of the shores would provide their people with iron slabs or plates to form the bottoms of the kilns in which the weeds are burned. This would prevent the admixture of earthy matters, sand, and stones, which is unavoidable in the present method of burning, and render the introduction of these for the purpose of adulteration quite inexcusable. These and a few other minor details would greatly increase the quantity and quality of the kelp made in the Western Islands of Scotland. Little or nothing will be done in the way of improvement, however, until the proprietors of the shores take a personal interest in the trade, and expend some capital in the erection of buildings and the purchase of such simple apparatus as the islanders are capable of using with advantage. The proprietors would thus confer a great benefit upon their poor tenants, and their estates would soon yield largely augmented returns. There is little danger of the quantity of iodine produced proving greater than the consumption, as, from the value of the compounds of this element in medicine, the demand for it must steadily increase; while the numerous and important applications of potash-salts in the arts have already rendered the production of these compounds far inferior to the demand.

If the owners of the kelp-bearing estates would combine and appoint a kind of commission to visit the different islands in order to investigate into the matter, and to give hints to the kelpers, much good might, I think, be effected. Much might also be done in the way of instructing the kelpers by the iodine-makers' agents, if these gentlemen were themselves thoroughly initiated into the chemical principles involved in the production of kelp. The great aim, in my opinion, however, as mentioned in a former part of this paper, should be to substitute a loose unfused ash or charred weed for the ordinary kelp prepared at a high temperature, with a view to

prevent much of the volatilization of iodine which appears to occur, and the production of sulphides and other sulphur compounds which cause a great waste of vitriol in the extraction of the iodine. I hope that this paper may have the effect of at least attracting attention to this highly important subject.

PROCEEDINGS OF SOCIETIES.

Royal Society.

Notes of Researches on the Poly-Ammonias.—No. VI. New Derivatives of Phenylamine and Ethylamine. By A. W. Hofmann, LL.D., F.R.S. &c.

[Received June 9, 1859.]

Some time ago* I communicated to the Royal Society some results obtained in studying the action of dibromide of ethylene upon phenylamine. The principal product of this reaction was found to be a well-defined crystalline compound with basic characters. By the analysis of the base itself, and of several of its combinations, it had been proved that the formula

$$C_{16}H_9N = \left.\begin{matrix}(C_4H_4)''\\ C_{12}H_5\end{matrix}\right\} N$$

is the simplest atomic expression for the new substance; but the action of iodide of methyle and of ethyle upon this body having given rise to compounds

$$C_{34}H_{21}N_2I = \left.\begin{matrix}C_{16}H_9N\\ C_{16}H_9N\end{matrix}\right\} C_2H_3I$$

and

$$C_{36}H_{23}N_2I = \left.\begin{matrix}C_{16}H_9N\\ C_{16}H_9N\end{matrix}\right\} C_4H_5I,$$

I was induced to assume the formula

$$C_{32}H_{18}N_2 = \left.\begin{matrix}(C_4H_4)''\\ (C_{12}H_5)_2\end{matrix}\right\} N_2$$

as representing the true constitution of the basic body, which thus appears as a diammonia, in which 2 equivs. of hydrogen are replaced by 2 equivs. of phenyle, and 4 equivs. of hydrogen by 2 molecules of diatomic ethylene.

This view involves the existence of a basic compound,

$$C_{28}H_{16}N_2 = \left.\begin{matrix}(C_4H_4)''\\ (C_{12}H_5)_2\\ H_2\end{matrix}\right\} N_2,$$

i.e. of a diphenyl-diamine in which only one molecule of diatomic ethylene has been substituted for hydrogen.

* Chem. Gaz. vol. xvi. p. 373.

Experiment has not failed to realize the body pointed out by theory. A mixture of dibromide of ethylene with a large excess of phenylamine (1 vol. of dibromide of ethylene and 4 vols. of phenylamine) rapidly solidifies to a crystalline mass. Treatment with water removes from this mixture a very considerable proportion of hydrochlorate of phenylamine, leaving a brown resinous substance, which gradually but imperfectly solidifies. This substance forms a hydrochlorate which is difficultly soluble in concentrated hydrochloric acid, and which may be readily purified by repeated crystallizations from boiling alcohol. The pure hydrochlorate dissolved in water, and mixed with potassa or ammonia, furnishes the free base, which generally separates as an oil, rapidly solidifying into a crystalline substance. This may be further purified by repeated crystallizations from diluted alcohol.

Analysis, in fact, assigns to this body the formula

$$C_{28}H_{16}N_2 = \left.\begin{matrix}(C_4H_4)''\\(C_{12}H_5)_2\\H_2\end{matrix}\right\}N_2,$$

which was confirmed by the analysis of the dichloride—

$$\left[\left.\begin{matrix}(C_4H_4)''\\(C_{12}H_5)_2\\H_4\end{matrix}\right\}N_2\right]''Cl_2,$$

and of the platinum-salt—

$$\left[\left.\begin{matrix}(C_4H_4)''\\(C_{12}H_5)_2\\H_4\end{matrix}\right\}N_2\right]''Cl_2,\ 2PtCl_2.$$

The formation of the new body is obvious:

$$4\left[\left.\begin{matrix}C_{12}H_5\\H_2\end{matrix}\right\}N\right] + (C_4H_4)''Br_2 = \left.\begin{matrix}(C_4H_4)''\\(C_{12}H_5)_2\\H_2\end{matrix}\right\}N_2 + 2\left(\left[\left.\begin{matrix}C_{12}H_5\\H_3\end{matrix}\right\}N\right]Br\right).$$

Phenylamine. — Dibromide of Ethylene. — Ethylene-diphenyl-diamine. — Bromide of Phenyl-ammonium.

This substance differs in its physical characters essentially from the base containing 2 molecules of ethylene. The former is very soluble in alcohol and ether, the latter being very difficultly soluble; its fusing-point is 59°, the fusing-point of the latter being 157°.

In order finally to establish the relation between the body which forms the subject of this note and the base previously described, it remained to prove experimentally that the former, when submitted to the action of dibromide of ethylene, may be readily converted into the latter. Nothing is easier than to accomplish this transformation, which, in the presence of alcohol, is rapidly effected at the temperature of boiling water.

Treatment of the product of digestion with water removes the dichloride of ethylene-diphenyl-diammonium, the diethylene-diphenylamine remaining dissolved in the excess of dibromide of ethylene, from which it may be readily extracted by hydrochloric acid.

Preparation of the substance in a state of purity, and comparison of its properties with those of the body previously obtained, established beyond a doubt the transformation, which resolves itself into a simple process of substitution—

$$2\left[\begin{matrix}(C_4H_4)''\\(C_{12}H_5)_2\\H_2\end{matrix}\right\}N_2\Bigg] + (C_4H_4)''Br_2 = \left.\begin{matrix}(C_4H_4)''\\(C_{12}H_5)_2\end{matrix}\right\}N_2 + \left[\begin{matrix}(C_4H_4)''\\(C_{12}H_5)_2\\H_4\end{matrix}\right\}N_2\Bigg]''Br_2.$$

Ethylene-diphenyl-diamine being a secondary diamine, it was not without interest to replace the two remaining hydrogen-equivalents by two monatomic molecules. On digesting the base with iodide of ethyle some hours at a temperature of 100°, a beautiful iodide was obtained, crystallizing in well-defined prisms, difficultly soluble in water, but more soluble in alcohol.

This substance contains

$$C_{36}H_{28}N_2I_2 = \left[\begin{matrix}(C_4H_4)''\\(C_4H_5)_2\\(C_{12}H_5)_2\\H_2\end{matrix}\right\}N_2\Bigg]''I_2.$$

Treatment with potassa separates from this iodide the base as a crystalline body fusing at 70°, and resembling in many respects the previous base. It contains

$$C_{36}H_{24}N_2 = \left.\begin{matrix}(C_4H_4)''\\(C_4H_5)_2\\(C_{12}H_5)_2\end{matrix}\right\}N_2,$$

and forms a beautiful platinum-salt crystallizing in needles of the formula

$$[C_{36}H_{26}N_2]''Cl_2, 2PtCl_2.$$

The deportment of phenylamine under the influence of dibromide of ethylene gives a fair illustration of the nature of the substances which are generated, under the influence of diatomic molecules, from primary aromatic monamines.

To complete the study of this subject, I have examined, moreover, the action of dibromide of ethylene upon ethylamine, as a representative of the monamines containing an ordinary alcohol-radical.

Dibromide of ethylene acts upon ethylamine even in the cold, the products of the reaction varying according to the relative proportions of the two bodies, and according to the temperature. Among other products invariably occur the two bromides corresponding to the two salts of the phenyl-compounds mentioned in the previous paragraphs.

These substances are the

Dibromide of ethylene-diethyl-diammonium, $\left.\right\}C_{12}H_{18}N_2Br_2 = \left[\begin{matrix}(C_4H_4)''\\(C_4H_5)_2\\H_4\end{matrix}\right\}N_2\Big]''Br_2$, and

Dibromide of diethylene-diethyl-diammonium, $\left.\right\}C_{16}H_{22}N_2Br_2 = \left[\begin{matrix}(C_4H_4)_2''\\(C_4H_5)_2\\H_2\end{matrix}\right\}N_2\Big]''Br_2$.

I have fixed the composition of the former compound by the analysis of the dibromide of the dichloride and of the base itself, all of which are remarkably well-defined crystalline bodies, and that of the latter by the examination of a well-defined platinum-salt.

The first base, separated by the action of anhydrous baryta from the dry bromide, distils as an oily liquid of a powerfully ammoniacal odour, which solidifies into a brittle crystalline mass not unlike fused stearic acid. The composition of the body is remarkable. It contains

$$C_{12}H_{18}N_2O_2 = \left[\begin{matrix}(C_4H_4)''\\(C_4H_5)_2\\H_4\end{matrix}\right\}N_2\Big]''O_2,$$

and thus constitutes the dioxide of the diatomic metal, ethylene-diethyl-diammonium.

The second base is liquid, and boils at 185°. It is easily obtained from the dibromide, which, being extremely soluble, may be readily separated from the bromide of the first body. I have experimentally established that this body may be readily procured by the action of dibromide of ethylene upon the dioxide previously mentioned.

The dioxide,

$$C_{12}H_{18}N_2O_2,$$

presents considerable interest in a theoretical point of view. I have determined the vapour-density of this compound by Gay-Lussac's process. Experiment gave the number 2·26. Assuming that the molecule of the body under examination corresponds to 4 volumes of vapour, the theoretical density is 4·62.

The extraordinary discrepancy between theory and experiment may be removed in two ways: viz. either by halving the formula, or by assuming that the molecule of the dioxide of ethylene-diethyl-diammonium corresponds to 8 volumes of vapour, in either of which cases the theoretical density becomes 2·31, closely agreeing with the experimental number 2·26.

I shall discuss the vapour-densities of the diammonias somewhat more fully in a future communication; but I cannot refrain from pointing out even now, that, by dividing the formula by 2, we arrive at an expression containing 1 equiv. of oxygen (O=8), which, in the eyes of those who consider the number 16 as the true molecular value of oxygen, must appear perfectly inadmissible.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Ozone upon Organic Compounds.

By E. VON GORUP-BESANEZ.

THE author has published an account of a series of experiments in which he exposed organic bodies to the action of ozone, and investigated the products of oxidation.

Cyanide of Potassium in aqueous solution attracts ozone greedily, and becomes converted into cyanate of potash.

Uric Acid absorbs ozone with the most greediness of any of the substances upon which the author operated. It becomes converted into allantoine and urea. Oxalic acid could not be detected in the products of oxidation.

Urea, *Alloxan*, *Alloxantine*, *Creatine*, *Leucine*, *Hippuric Acid*, *Amygdaline*, and *Salicine* are scarcely or not at all acted upon by ozone.

Albuminous substances, and especially white of egg, behave in a remarkable manner towards ozone. If a current of strongly ozonized air be conducted into an aqueous solution of albumen, very perceptible changes soon occur. The solution becomes turbid, and at the same time changes its colour, presenting a reddish aspect by reflected light, while by transmitted light it appears greenish yellow. It consequently exhibits the phænomenon of dichroism, although but in a slight degree. The froth rising from the solution is soon permeated by numerous white coagula, which, when pressed between the fingers, in order to remove the enclosed air, shrivel up into tenacious, greyish-white, fibrous masses. These, in their whole behaviour, exhibit an unmistakeable resemblance to fibrine, although they are not soluble in nitric acid, at least as appeared from one experiment. The formation of these coagula increases up to a certain point, but then suddenly diminishes, those already formed being also dissolved, whilst the colour of the fluid becomes lighter again at the same time. From this point, the action of the ozone

being continued, no other phænomena are observed, except that the frothing constantly diminishes, and the fluid becomes clearer in the same proportion. At first the absorption of the ozone is very rapid, but it afterwards becomes more sluggish, and finally ceases altogether, which the author could only ascertain by putting the fluid towards the end of the experiment into balloons with ozonized air, and trying whether or not the air in the balloons had lost its ozone-reaction after being agitated with the fluid for 24—36 hours. If the former were the case, the experiment was stopped. After the completion of the experiment the fluid no longer frothed, was only rendered turbid by a few flakes which settled readily, and possessed a slightly acid reaction; it continues perfectly clear when filtered while boiling, and can no longer be precipitated either by mineral or organic acids, or by metallic salts, with the exception of basic acetate of lead; even ferrocyanide of potassium does not precipitate the solution, but alcohol produces a strong turbidity. This solution consequently no longer contains albumen. The concentrated solution deposits no crystals even by long standing; when completely evaporated on the water-bath, it leaves a brownish, extract-like residue, which is only partially soluble in alcohol. The alcoholic solution, which has an acid reaction, leaves a syrupous residue when evaporated. It does not contain urea. Neither leucine, nor other well-characterized bodies could be found in the alcoholic extract. The portion of the residue insoluble in alcohol, is very similar in its external characters to the portion of the residue of urine which is insoluble in alcohol; under the microscope it exhibits no trace of crystallization, and is perfectly soluble in water. Its aqueous solution has a distinct acid reaction, and, when heated upon platinum-foil, leaves a brownish residue, which, when further heated, becomes inflated with evolution of an odour like that of burnt horn, takes fire, and leaves behind a voluminous coal of a fused appearance, which burns with great difficulty, and finally a very small residue of ashes. It is not precipitated by mineral acids and acetic acid, or by ferrocyanide of potassium and solution of sulphate of alumina and potash; tannic acid, on the contrary, produces a strong white plaster-like precipitate. Acetate of lead, bichloride of mercury, salts of peroxide of copper, and even lime-water produce a slight turbidity in the concentrated solution; nitrate of silver causes a yellowish turbidity, and on boiling the solution mixed with silver becomes brownish red. Nor could any well-characterized bodies be detected in the insoluble part of the residue. The author sought in vain for sugar especially, both in the aqueous and alcoholic extracts.

The most important result derived from these experiments is that albumen undergoes a radical alteration, in consequence of which it loses especially the property of being precipitated by all those reagents which generally precipitate albumen and the albuminates. This result has a physiological interest, because the product formed by the action of ozone upon albumen agrees so closely with Lehmann's peptones, the products of the conversion of the albuminates

by the ferment of the stomach. In connexion with this it is to be observed, that the solutions of the peptones have an acid reaction, and are no longer precipitated by the precipitants of the albuminates. Even the fact that at the commencement of the action of ozone upon albumen a body is produced possessing so great an external resemblance to coagulated fibrine, appears to be in a high degree worthy of notice.

Caseine.—The action of ozone upon soluble caseine is not less energetic than upon albumen; but in this no such characteristic phænomena are observed as in the latter. Neither change of colour nor formation of coagula takes place, but the fluid, which at first exhibits a milky turbidity, gradually becomes clearer, until at the conclusion of the experiment it presents a similar appearance to that obtained from albumen.

When the action of the ozone has continued for some time, the fluid is no longer precipitated by acetic acid, so that it does not contain any ordinary caseine; but if it be heated to boiling, it coagulates like solution of albumen, and it is also precipitated by nitric acid. The caseine is therefore at this period converted into a body with the properties of albumen. Subsequently this is also destroyed, and after the conclusion of the experiment no albuminate is contained in the clear filtered fluid. When evaporated, it leaves a residue which perfectly agrees in every respect with that of the oxidized albumen.

The author also found that when milk itself is treated with ozonized air, the caseine entirely disappears in the course of a few days, whilst the fat of the milk is only destroyed very slowly, and not entirely even in several weeks. When no further reaction takes place and the fluid is evaporated, an abundant crystallization of sugar of milk is obtained.

From this it follows that of all the constituents of milk the caseine is most easily acted upon by ozone, but that the sugar of milk is not attacked at all.

Fibrine.—Fresh, pure, well-washed blood-fibrine, prepared from pig's blood, proved to be perfectly indifferent towards ozone.

Pure, colourless Bone-gelatine, and also pure *Bile* freed from mucus, colouring matter, and fats, is not acted upon by ozone.

Starch, *Cane-sugar*, and *Inosite* are also indifferent towards ozone.

Amylic Alcohol takes up ozone; its odour passes by degrees into that of valeraldehyde. The fluid afterwards becomes acid, and then contains valerianic acid.

Oil of Cinnamon takes up ozone instantaneously, but undergoes no apparent change thereby; it behaves rather like an excellent bearer of ozone, that is to say, as a body which takes up ozone, without immediately combining with it, and parts with it again to other bodies. In fact, by means of the ozonized oil the author could produce all those oxidizing actions which characterize ozonized turpentine; it possessed especially a very great power of decolorizing indigo.

Tannic Acid is one of those substances which take up ozone

most greedily. If ozonized air be conducted into a solution of tannic acid, it gradually becomes darker up to a certain point, until its colour has become a deep brownish red; but from this point it again becomes paler, and at the conclusion of the experiment exhibits only a slight wine-yellow colour. The ozone is taken up equally rapidly and completely to the end of the experiment; but if the fluid be then evaporated, a very small brownish residue is left, which, even when 15 grms. of tannic acid were employed in the experiment, was not in sufficient quantity to enable further experiments to be made. Tannic acid, therefore, appears to undergo complete combustion by ozone, with formation of oxalic acid and of a body which reduces peroxide of copper in alkaline solution to the state of protoxide, exactly like sugar, even when very gently heated, which is not the case with unaltered tannic acid. The author attempted to ferment this, but with a negative result.

In conclusion, the author calls particular attention to the fact that, with the exception of tannic acid, all truly fermentiscible substances behaved negatively with ozone,—such are urea, creatine, leucine, bile, hippuric acid, sugar, amygdaline, and salicine. From this it might be concluded that a conversion of these bodies, as far as they occur in the organism, is likewise assisted only by processes of splitting, but not by direct oxidizability in presence of free alkalies or of free acids, which is already proved with regard to certain bodies, and probable with regard to others. A further series of experiments with which the author is occupied will settle this point. —Liebig's *Annalen*, cx. p. 86.

On Chlorous Acid. By J. Schiel.

The author shows that chlorous acid may be prepared without the least danger of explosion, when nothing but pure chlorate of potash and pure nitric acid are employed for the purpose. A small amount of sulphuric acid has no injurious action. The author has operated upon several pounds of chlorate of potash at once, and the temperature of the water-bath frequently rose to 140° F. without producing any explosion.

The author usually employs a mixture of 2 parts of chlorate of potash, 3 parts of nitric acid of spec. grav. 1·30, 0·6 to 0·8 part of cane-sugar and 3 to 4 parts of water; it is not necessary to pulverize the sugar or chlorate of potash, or to mix them before they are put into the bottle, as is recommended by Millon, when tartaric acid is employed, with which, however, it is equally unnecessary.

At 46°—50° F. water takes up more then ten times its volume of chlorous acid; the solution is of a deep yellowish-red colour, almost like a somewhat dilute solution of bichromate of potash. It is of the more value as a disinfecting and bleaching liquid, as it may be kept for a considerable time without decomposition. The bleaching power of the concentrated acid is nearly fourteen times that of chlorine.

The oxidizing action of an equivalent of chlorous acid is to that

of chlorine as 4 : 1. Aqueous chlorous acid dissolves finely divided amorphous phosphorus almost instantaneously. When a strong glass tube is blown into a bulb of about 20—30 cubic centims. capacity, and drawn out on each side of the bulb into long fine points, the bulb may be easily filled with chlorous acid by fastening it by means of a cork to an apparatus from which chlorous acid is slowly evolved. When the bulb is filled, which requires some time, and which may be easily ascertained by the colour, the fine points may be carefully sealed without producing any decomposition of the acid in the bulb. In a bulb of this kind the gaseous acid is very quickly decomposed in direct sunlight, but often remains undecomposed for several days in different light. The presence of a trace of moisture appears to facilitate the decomposition.

Of all the salts of chlorous acid, the lead-salt is the most remarkable and interesting. Its property, already described by Millon, of igniting sulphur when rubbed with it, leads to a technical application of this salt.

Considerable quantities of a dry mixture of chlorite of lead and sulphur, or a metallic sulphuret belonging to the series of electronegative metals, such as sulphuret of gold, &c., cannot be left to themselves, as the mixture, after standing for some time, ignites spontaneously with explosion. The chlorites are well known to undergo a slow decomposition by the carbonic acid of the air; the chlorous acid set free oxidizes the sulphur, and the mixture is thus gradually heated to a temperature which causes its explosion. By the fulfilment of certain conditions, mixtures may be prepared which explode spontaneously with great force almost with a certain regularity at a given time.

For the preparation of the lead-salt, the concentrated aqueous solution of the acid is almost neutralized by baryta or milk of lime. The slightly acid solution is filtered and precipitated, without previous concentration, with a solution of nitrate of lead. One litre of a concentrated solution of chlorous acid gives 120—140 grms. of chlorite of lead. If the solution of chlorite of lime be heated to 122°—140° F. before it is mixed with the solution of nitrate of lead, the chlorite of lead is obtained in larger crystalline scales.

Chlorite of lead is decomposed with a considerable explosion at as low a temperature as 212° F. (at 259° F. according to Millon).

The author has obtained various compounds of chlorous acid with lead and chloride of lead. If the acid be neutralized with potash, the precipitated lead-salt has the composition PbO, ClO^3, namely,—

Oxide of lead	65·23
Chlorous acid	34·56
Loss.....	0·21

From the mother-liquor filtered from the lead-salt, small, slightly yellow, acicular crystals are in course of time deposited on the walls of the vessel; these are rather difficult of solution in water, detonate slightly when triturated with sulphur, and may be regarded as a compound of chlorite of lead with chloride of lead. Dilute nitric acid

evolves chlorous acid from them. Their analysis gave—

Lead.....	65·24
Chlorine	21·41
Oxygen	13·35

The formula $2(PbO, ClO^3)+PbCl$ requires—

Lead.....	64·75
Chlorine	22·02
Oxygen	13·25

But as a general rule crystals are obtained of the following composition:—

Lead	66·91	67·27
Chlorine ..	20·67	21·16
Oxygen ..	12·42	12·57

which corresponds with the formula $3(PbO, ClO^3), 2PbCl+\frac{1}{2}PbO$.

The oxide of lead expressed in the formula is probably only to be regarded as intermixed and originating from nitrate of lead carried down with the compound.—Liebig's *Annalen*, cix. p. 317.

On the Solubility of Bone-earth from various Sources in Solutions of Chloride of Ammonium and Common Salt. By JAMES BIRNEY, *Student in the Evening Class for Practical Chemistry, Museum of Irish Industry*.*

The following experiments were undertaken with the view of ascertaining whether the insoluble phosphate in guano and in superphosphate, made from bones and from coprolites, had the same money value.

This problem appeared to be only capable of solution by ascertaining the relative solubility of the bone-earth from these various sources in some menstruum. I selected as the solvent a solution of chloride of ammonium of known strength, and determined first of all the solvent powers of this saline solution on pure bone-earth artificially prepared. For this purpose I made the following experiments:—The bone-earth employed in each experiment, after being precipitated, washed, and dried, was ignited for a considerable time over a gas-light, and afterwards coarsely powdered. It was digested for twenty-four hours in the chloride of ammonium solution; the quantity dissolved was determined by collecting the undissolved portion upon a filter, and washing it until the wash-water did not contain a trace of chlorine. It was subsequently dried, ignited, and weighed, and the difference in weight between the undissolved portion and the bone-earth employed, was the quantity dissolved by the saline solution.

I. 16·930 grs. of the artificial bone-earth so treated were digested in 2000 grs. of a chloride of ammonium solution containing 20 grs.

* Communicated by the Author; having been read at the Meeting of the British Association at Aberdeen, September 14, 1859.

of the ammoniacal salt; the undissolved portion weighed 16·395 grs.; the quantity dissolved was therefore 0·535 gr.=3·160 per cent.

II. 15·265 grs. of the artificial bone-earth were digested in 2000 grs. of the chloride of ammonium solution employed in the preceding experiment; the undissolved portion weighed 14·883 grs.; the quantity dissolved was therefore 0·382 gr.=2·502 per cent.

III. 16·367 grs. of the artificial bone-earth were digested in one-half the quantity (1000 grs.) of the same chloride of ammonium solution which was employed in the two preceding experiments; the undissolved portion weighed 15·756 grs.; the quantity dissolved was therefore 0·611 gr.=3·733 per cent.

IV. 18·819 grs. of the artificial bone-earth were digested in 1000 grs. of the chloride of ammonium solution employed in the last experiment; the undissolved portion weighed 18·198 grs.; the quantity dissolved was therefore 0·621 gr.=3·299 per cent.

V. 16·990 grs. of the artificial bone-earth were digested in 1000 grs. of an ammoniacal solution containing 25 grs. of chloride of ammonium; the undissolved portion weighed 16·553 grs.; the quantity dissolved was therefore 0·437 gr.=2·572 per cent.

VI. 15·210 grs. of the artificial bone-earth were digested in 1000 grs. of a chloride of ammonium solution of the same strength as in the preceding experiment; the undissolved portion weighed 14·643 grs.; the quantity dissolved was therefore 0·567 gr.=3·727 per cent.

VII. 16·408 grs. of the artificial bone-earth were digested in 4000 grs. of a chloride of ammonium solution containing 4 grs. of the ammoniacal salt; the undissolved portion weighed 15·788 grs.; the quantity dissolved was therefore 0·620 gr.=3·788 per cent.

VIII. 16·155 grs. of the artificial bone-earth were digested in 1000 grs. of a chloride of sodium solution containing 10 grs. of the sodium salt; the undissolved portion weighed 15·680 grs.; the quantity dissolved was therefore 0·475 gr.=2·940 per cent.

IX. 17·212 grs. of the artificial bone-earth were digested in 1000 grs. of the chloride of sodium solution employed in the last experiment; the undissolved portion weighed 16·895 grs.; the quantity dissolved was therefore 0·317 gr.=1·853 per cent.

These results confirm those recorded by Baron Liebig in his recent work on agriculture, which has been issued since I completed this part of my investigation: he states that phosphate of lime is more soluble in a solution of chloride of ammonium than in one of chloride of sodium; also that the quantity of phosphate of lime does not appear to be regulated by the quantity of ammoniacal salt in the solution; but so far as my experiments have extended, the results would even prove that it is not regulated by the quantity of solution, which is improbable.

The following experiments were made with ground bones: the bones were first digested in distilled water. In the first experiment, the aqueous solution was filtered whilst the greater part of the gelatine was still undecomposed; in the second, the solution was not filtered until the solution ceased to have a putrid smell, and therefore until the last decomposition products had been formed.

The residue of bone-earth which remained in each case was subsequently digested in a solution of chloride of ammonium for twenty-four hours; the solution was then filtered, the phosphoric acid was determined, both in the aqueous and ammoniacal solutions, in the following way:—the solutions were evaporated to dryness and ignited until the ammoniacal salts were expelled; the residue in each case was then dissolved in a little hydrochloric acid, this solution was then neutralized by ammonia; acetic acid was then added in excess, and lastly, oxalate of ammonia. After standing twenty-four hours, the solution was filtered from the precipitated oxalate of lime; the filtrate was concentrated by evaporation, if necessary; and finally, the phosphoric acid was precipitated from it as ammonio-phosphate of magnesia by adding to the solution chloride of ammonium, ammonia, and sulphate of magnesia. The ammonio-phosphate of magnesia was collected, dried, ignited, and weighed as pyrophosphate of magnesia.

I made two determinations of the nitrogen in the bones; the mean of the two experiments gave 2·68 per cent. of nitrogen, which is equal to 3·26 of ammonia, or 10·23 of chloride of ammonium.

I. 100 grs. of the ground bones were digested in 4000 grs. of distilled water; the pyrophosphate of magnesia obtained by precipitating the phosphoric acid from the solution in the way described, weighed 3·700 grs.=5·161 $3CaO, PO^5$.

The residue was digested in 4000 grs. of a solution of chloride of ammonium containing 40 grs. of the ammoniacal salt; the $2MgO, PO^5$ obtained by precipitating the phosphoric acid from the solution in the way described, weighed 1·50 gr.=2·09 grs. $3CaO, PO^5$.

II. 100 grs. of the ground bones were digested in 4000 grs. of distilled water; the $2MgO, PO^5$ obtained by precipitating the phosphoric acid from the solution in the way described, weighed 1·40 gr. =1·950 gr. $3CaO, PO^5$.

The residue was digested in 8000 grs. of a solution of chloride of ammonium containing 80 grs. of the ammoniacal salt; the $2MgO, PO^5$ obtained by precipitating the phosphoric acid from the solution in the way described, weighed 0·357 gr.=0·496 $3CaO, PO^5$.

The great difference in the quantity of bone-earth dissolved out by the ammoniacal solutions in the two experiments, is owing, I believe, to the bones not being in a uniform state of division; but there is one fact established, I think, by these experiments, and that is that bone-earth is more soluble in a solution of gelatine than in one of chloride of ammonium; for if the nitrogen in the nitrogenous substances of the bones had taken the form of ammonia, it would only have yielded 3·26 of ammonia, or 10·23 of chloride of ammonium; yet the mere digestion of the bones in distilled water rendered (in the first experiment) 5·161 per cent. of bone-earth soluble, whereas 40 grains of chloride of ammonium rendered only 2·09 grs. of bone-earth soluble in the residue which remained after digesting the bones in distilled water.

I made two separate experiments with ground coprolites; in one experiment I employed 35·12 grs., and in the other 33·66 grs. of the

coprolites. I digested each portion in 4000 grs. of a solution of chloride of ammonium containing 40 grs. of the ammoniacal salt; the phosphoric acid was precipitated from the solutions in the way described in the experiments on bones, but the quantity which had been dissolved out by the ammoniacal solution in both experiments was so small that it did not admit of being weighed.

In the next experiment which I made, the bone-earth was obtained from some superphosphate made from bones. The superphosphate was digested in distilled water, and washed until the soluble phosphate was removed; the residue was then dried at a temperature of 212° F.

16·40 grs. of the dry residue were digested in 4000 grs. of a solution of chloride of ammonium containing 40 grs. of the ammoniacal salt; the $2MgO, PO^5$ obtained by precipitating the phosphoric acid from the solution in the way previously described, weighed 0·225 gr.=0·313 of $3CaO, PO^5$=1·908 per cent.

In the next experiment the bone-earth was obtained from Peruvian guano; the guano was digested in distilled water, and washed until all the soluble portion was removed; the residue was then dried at a temperature of 212° F.

35·863 grs. of the dry residue were digested in 4000 grs. of a solution of chloride of ammonium containing 40 grs. of the ammoniacal salt; the $2MgO, PO^5$ obtained by precipitating the phosphoric acid in the way already described, weighed 0·357 gr.=0·496 gr. of $3CaO, PO^5$=1·383 per cent.

Further experiments will be required to establish the relative solubility in ammoniacal solutions of the insoluble phosphates in different manurial substances, but these experiments may be regarded, I hope, as a slight contribution towards the subject.

Baron Liebig, in his recent work on agriculture, has shown that many substances, especially ammoniacal salts and chloride of sodium, act beneficially on soils, not only by serving themselves as food for plants, but also by their solutions dissolving some of the insoluble constituents of soils which are required by plants; these and similar experiments will therefore have also a value in this direction.

I am still occupied in studying the action on rocks and soils of solutions of ammoniacal and soda salts; it may be possible to determine by the aid of these saline solutions, whether a soil does or does not contain a sufficient amount of phosphates; for, according to Baron Liebig, very dilute solutions of these salts take up phosphoric acid from a soil which contains earthy phosphates in *excess*, and that this dissolved acid is again given up by this solution to a similar soil which is *not* already saturated with phosphoric acid.

My experiments on the solubility of phosphoric acid in solutions of chloride of ammonium, show that the method which Dr. Macadam has given, in his paper on the analysis and valuation of manures for the estimation of phosphate of lime, and which is, I believe, the plan followed by many of the analytical chemists who devote themselves to the analysis of manures, is open to very grave objections. According to my experiments, phosphate of lime dissolves in solu-

tions of chloride of ammonium in the proportion of 0·5 gr. for every 16 grs. when digested in 1000 or 2000 grs. of fluid for 24 hours; and it must be remembered that the phosphate of lime in my experiments had been strongly ignited, and was very coarsely powdered; it may therefore be fairly assumed that freshly precipitated phosphate of lime will dissolve not only with much greater facility, but also in much larger quantities in solutions of chloride of ammonium; and it is under these conditions that phosphate of lime is estimated in manures by Dr. Macadam and others; it is not difficult to perceive that this mode of estimating phosphates must give very incorrect results.

These experiments were conducted in the laboratory of the Museum of Irish Industry, under the direction of Mr. Galloway.

On the Chinone Group. By O. Hesse.

Kinic acid dissolves in concentrated sulphuric acid with evolution of gas, and sulphurous acid is evolved on the application of heat. The author has found that the sulphurous acid only makes its appearance when the fluid is heated to about 212° F.; the gas evolved below this temperature is carbonic oxide. Even before the evolution of sulphurous acid, the fluid contains a conjugate sulphuric acid. This is best prepared as follows:—

Fused or finely powdered kinic acid is put into a spacious vessel. Fuming sulphuric acid is poured upon this, until a further addition causes no considerable evolution of gas. Towards the conclusion of the operation the vessel is gently heated, and after cooling, the brown syrup is diluted with water and neutralized with carbonate of baryta; the dark brown clear solution is then evaporated in the water-bath until it crystallizes. The baryta-salt, which crystallizes in fine needles, is placed between layers of bibulous paper to free it from the dark-coloured mother-liquor. The salt cannot be obtained colourless by recrystallization, or even by treatment with animal charcoal; it was, however, prepared of a light flesh-colour, by allowing a portion of the salt to crystallize first of all, and then carefully evaporating the mother-liquor of this in the water-bath. If the baryta-salt separates slowly, it is obtained in beautiful monoclinic prisms. It is rather difficult of solution in cold water and cold alcohol, readily soluble in boiling water, sparingly in boiling alcohol, and insoluble in æther. During dry distillation it furnishes fumes of a penetrating odour (sulphuric acid), hydrochinone, and chinone-hydrochinone; water is also evolved, and there remains a carbonaceous mass, which retains the form of the substance employed. The solution possesses a brownish colour by transmitted, and a fine violet-blue colour by reflected light.

The solutions of the baryta-salt and of every soluble salt of the new acid, as also the latter itself, furnish with perchloride of iron a blue colour, which does not yield to that of indigosulphuric acid in beauty and intensity. Acetic acid, nitric acid, and even the access of air gradually destroy the colour; it also disappears

very readily by treatment with muriatic acid, sulphuric acid, tartaric acid, and solutions of the following salts: muriate of ammonia, chloride of barium, chloride of calcium, sulphate of magnesia, phosphate of soda, acetate of lead, and perchloride of iron. Heat also causes the colour to disappear. On cooling, the fluid becomes dark, and acquires a dingy colour. The analysis of the salt dried at the ordinary temperature under the exsiccator, gave,—

	Found.		Calculated.
	I.	II.	
C	15·5	..	12=15·08
H	2·9	..	12 2·52
Ba	28·5	28·4	2 28·75
S	13·8	..	4 13·41
O	..	..	24 40·24

When dried at a temperature of 212° F. this salt lost 10·8, 11·5, and 11·3 per cent.=6 equivs. water. At a temperature above 248° F. it lost further 3·77, 3·0, 3·4, and 3·5 per cent.=2 equivs.

The salt dried at 212° F. consequently has the formula

$$C^{12}H^{4}Ba^{2}S^{4}O^{16}+2HO,$$

and that dried at 320° F., the formula

$$C^{12}H^{4}Ba^{2}S^{4}O^{16}.$$

The free acid may be obtained from this baryta-salt by means of an equivalent quantity of sulphuric acid. It may also be prepared by the decomposition of the following lead-salt by means of sulphuretted hydrogen. The author calls it bisulphohydrochinonic acid, because its formula, $C^{12}H^{6}S^{4}O^{16}$, contains the elements of hydrochinone and sulphuric acid. The author assumes the formula of kinic acid to be $C^{14}H^{12}O^{12}$, and explains the production of the acid by the following equation:—

$$C^{14}H^{12}O^{12}+2.S^{2}O^{6}=C^{2}O^{2}+C^{12}H^{6}S^{4}O^{16}+6HO.$$

Bisulphohydrochinonate of Lead, $C^{12}H^{4}Pb^{2}S^{4}O^{16}+2PbHO^{2}$.—Neutral acetate of lead precipitates the solution of the baryta-salt. The precipitate is voluminous, and soon becomes converted into somewhat yellowish, silky, microscopic crystals. It is nearly insoluble in water and acetic acid, readily soluble in nitric acid, and precipitable in an amorphous form from these solutions by ammonia. When heated it becomes lemon-yellow. Analysis:—

	Found.	Calculated.
Carbon	10·5	12=10·04
Hydrogen	1·1	6 0·84
Lead	58·2	4 57·87
Sulphur	..	4 8·93
Oxygen	..	20 22·32

The Ammonia-salt is obtained by decomposing the baryta-salt with carbonate of ammonia. It crystallizes from the concentrated solution in large crystals.

The Potash-salt, $C^{12} H^4 K^2 S^4 O^{16} + 3\,HO$, is obtained by saturating the free acid with carbonate of potash; the neutral salt is produced from a solution containing 2 equivs. of acid to 1 equiv. of carbonate. It possesses a saline, but not cooling taste, is readily soluble in cold and boiling water, and sparingly soluble in alcohol. It forms colourless prisms, the solution of which exhibits dichroism. The air-dried salt loses nothing in the exsiccator. It fuses at the temperature of decomposition.

The Lime-salt, $C^{12} H^4 Ca^2 S^4 O^{16}$, is obtained by precipitating the potash-salt with chloride of calcium. It is crystalline, and resembles the baryta-salt. The air-dried salt loses no water in the exsiccator.

The circumstance that the organic conjunct in this sulpho-acid possesses the composition of hydrochinone, induced the author to study the behaviour of this latter body towards sulphuric acid.

Hydrochinone is dissolved by fuming sulphuric acid with no considerable blackening and without evolution of gas. The solution, diluted with water, saturated with carbonate of baryta, and concentrated, furnished the baryta-salt of a new acid, different from the preceding one, to which the author gives the name of *sulphobihydrochinonic acid*. The salt is

Sulphobihydrochinonate of Baryta, $C^{24} H^5 BaS^2 O^{18}$; it forms concentrically grouped fine needles, the solution of which exhibits no dichroism. With perchloride of iron the solution gives a deep blue colour, which very soon disappears. With nitrate of silver it produces metallic silver; no crystals with bichloride of mercury; and with acetate of lead it gives colourless prisms after standing for a short time. Basic acetate of lead produces a voluminous precipitate in the solution of the baryta-salt. It is readily soluble in cold and hot water and alcohol, less soluble in absolute alcohol, and precipitable therefrom in white flakes by æther. In the exsiccator it loses 12 to 15 per cent. of water. When heated to 320° F. no loss of water could be detected, but it still appears to retain water of crystallization even at this temperature. The analysis of the salt dried over sulphuric acid, gave,—

	Found.	Calculated.
C	35·1	24 = 35·68
H	4·0	15 3·71
B	17·4	1 17·00
S	..	2 7·93
O	..	18 35·68

The solution of the free acid separated from the lead-salt acquired a dark colour by exposure to the air. If the barium in the formula of the baryta-salt be replaced by hydrogen, we obtain as the formula of the free acid $C^{24} H^{16} S^2 O^{18}$, and its production would consequently be

$$2(\underset{\text{Hydrochinone.}}{C^{12} H^6 O^4}) + 4\,HO + S^2 O^6 = C^{24} H^{16} S^2 O^{18}.$$

Liebig's *Annalen*, cx. p. 194.

On Chloropicrine. By Dr. L. Geisse.

The author treated chloropicrine, $C^2 Cl^3 NO^4$, with protacetate of iron. Chloropicrine was put into a spacious retort, the neck of which was turned upwards and connected with the lower extremity of a refrigerating apparatus. It was intimately mixed with iron-filings, and acetic acid was added to it by degrees in small quantities. The action is at first rather violent, but it afterwards becomes weaker, and must finally be assisted by a gentle heat. As soon as the odour of chloropicrine had completely disappeared, the entire contents of the retort was mixed with an excess of solution of soda, and boiled therewith for a considerable time. During this process a compound with a strong ammoniacal odour is volatilized, which, when collected in water in a receiver, communicates to this the same odour and a strong alkaline reaction.

This fluid was neutralized with muriatic acid, then evaporated as far as possible on the water-bath, and the salt, which on cooling set into a yellowish crystalline mass, deliquescent in the air, was purified by recrystallization from hot alcohol. The aqueous solution of the pure salt, mixed with a sufficient quantity of chloride of platinum, and evaporated on the water-bath, left a mass of beautiful yellow crystals, which were freed from the excess of chloride of platinum by washing with a mixture of alcohol and æther, and then dried in the air-bath between 176° and 194° F.

The analysis of this salt leads to the composition of platinochloride of methylammonium, $N\left\{\begin{matrix} C^2 H^3 \\ H^3 \end{matrix}\right. Cl, PtCl^2$; it gave,—

	Found.		Calculated.
	I.	II.	
C	4·9	..	2 = 5·0
H	2·5	..	6 2·5
N	..	..	1 5·9
Pt	41·9	42·1	1 41·6
Cl	..	..	3 45·0

The opinion already expressed that chloropicrine belongs to the methyle-series, is therefore not contradicted by this behaviour. Chloropicrine may indeed be regarded as chloroform in which H is replaced by NO^4. The iron not only effects a reduction of the group NO^4, but also causes the substitution of all the atoms of chlorine in the chloropicrine by hydrogen.

Chloropicrine, treated with sulphate of iron and an excess of solution of potash, furnished methylamine,

$$C^2 Cl^3 NO^4 + 12H = N\left\{\begin{matrix} C^2 H^3 \\ H^2 \end{matrix}\right. + 3HCl + 4HO.$$

Chloropicrine is also metamorphosed when it is treated, according to Piria's process, with sulphite of ammonia with the addition of carbonate of ammonia. An acid containing sulphur and chlorine is

produced, similar to those obtained from nitronaphthaline (Piria) and nitrotoluole (Hilkenkamp).

This conversion was best effected when the author conducted a current of sulphurous acid into a moderately concentrated alcoholic solution of potash in which a comparatively small quantity of chloropicrine had previously been dissolved. The metamorphosis of the chloropicrine takes place quietly and without any considerable evolution of heat, with deposition of a large quantity of sulphite of potash and chloride of potassium. The passage of the gas must, however, be interrupted the moment the alkali is completely neutralized. This point may easily be detected by the fluid suddenly acquiring a blood-red colour. At this moment also all the chloropicrine has disappeared. If sulphurous acid be still passed in, the red colour soon becomes yellow, and a stormy reaction immediately takes place, accompanied by so strong an evolution of heat, that the fluid, if not very well refrigerated, boils over. The fluid then has a strongly acid reaction, and no longer contains any of the desired product. The red alcoholic solution, filtered from the sulphite of potash and chloride of potassium, must be evaporated *in vacuo* over sulphuric acid; when it has attained the consistence of a syrup, it solidifies to a reddish-brown crystalline mass, which may be obtained perfectly pure by repeated crystallization from absolute alcohol. It is, however, difficult to prepare this compound in a perfectly dry state, and fit for analysis. Besides potash, carbon, and hydrogen, it contains sulphur and nitrogen.

If the alcoholic solution of this potash-salt be mixed with an aqueous solution of sulphate of copper, sulphate of potash and the excess of sulphate of copper are separated, whilst the copper-salt of the acid produced remains in solution, and may be obtained by the evaporation of the solution. The author could not continue the investigation of this salt, and only states with regard to it that it crystallizes in greenish tables, is readily soluble in water, and does not support a temperature of 176° F., whether in the dry state or in solution.—Liebig's *Annalen*, cix. p. 282.

ANALYTICAL CHEMISTRY.

On the Action of Air on Alkaline Arsenites. By John M'Donnell, *Student in the Evening Class for Practical Chemistry, Museum of Irish Industry*.*

Arsenious acid, dissolved in an alkaline solution, has been employed in the estimation of chloride of lime and other volumetric determinations. Fresenius has objected to this process on account of the liability of the arsenious acid, in the presence of an alkaline carbonate or free alkali, to become converted into arsenic acid; he states that a notable quantity of the arsenious becomes converted

* Communicated by the Author; having been read at the Meeting of the British Association at Aberdeen, September 14, 1859.

into arsenic acid if the alkaline arsenite be exposed to the air; if this were the case, it would either completely prevent it from being used, or it would render it less useful as a volumetric reagent. Mohr, on the other hand, denies that the arsenious acid oxidizes in the presence of alkalies or alkaline carbonates; he states that he kept an alkaline solution of arsenious acid for 10 months, and found at the expiration of that time that no arsenic acid had been formed. Still more recently Professor Croft of University College, Toronto, has investigated the subject; he states that a small quantity is formed, but that it is so very small that it does not prevent the employment of an alkaline solution of arsenious acid in accurate volumetric experiments.

I made the following experiments at the request of Mr. Galloway, to prove whether arsenious acid in an alkaline solution did really change by time and exposure to the air. For this purpose an alkaline solution of pure arsenious acid of known strength was kept 15 months in a two-quart bottle; the liquid filled the bottle only one-third, during that time the stopper was frequently removed from the bottle to introduce fresh air into it, and thus place the solution under the most favourable condition for the oxidation of the acid. At the expiration of the 15 months another alkaline solution of arsenious acid was made, of the same strength as the former solution, and the acid employed in the preparation of the two solutions was taken from the same sample. I weighed out, as soon as the second solution was made, 100 grs. of chloride of lime, triturated it with water, and finally made up the mixture to 10,000 grs.; 2000 grs. of this chloride of lime mixture was just sufficient to oxidize the arsenious acid in 310 grs. of the recently prepared solution. I repeated the experiment with other 2000 grs. of the same chloride of lime mixture, and found that it oxidized, as in the first experiment, the arsenious acid in 310 grs. of the recently prepared solution of the alkaline arsenite,—this is equal to 5·495 per cent. of available chlorine in the chloride of lime. I then employed other 2000 grs. of the same chloride of lime mixture, and found that it required of the alkaline solution of arsenious acid which had been kept 15 months, 315 grs. In a second experiment, 320 grs. of the arsenious acid solution was oxidized by 2000 grs. of the chloride of lime mixture. By the new solution, the chloride of lime contained 5·495 per cent. of chloride, and by the old solution,—

	Per cent.	Mean.
1st Experiment	5·583	5·627
2nd „ „	5·672	

The following experiments were then made. An alkaline solution of arsenious acid was freely exposed to sunlight for about 2 months; the solution was kept during that time in a stoppered bottle, which the solution only partly filled. At the end of that time, a fresh alkaline solution of arsenious acid was made; the acid employed in the preparation of the two solutions was taken from the same sample. When the new solution was made, I triturated 100 grs.

of chloride of lime with water, and finally made up the mixture to 10,000 grs.

2000 grs. of this chloride of lime mixture oxidized the arsenious acid in 1340 grs. of the solution which had been kept 2 months,—this is equal to 23·758 per cent. of chlorine. In a second experiment, other 2000 grs. of the same chloride of lime mixture required 1335 grs. of the same arsenite solution,—this is equal to 23·669 per cent. of chlorine. 2000 grs. of the same chloride mixture oxidized the arsenious acid in 1330 grs. of the fresh arsenite solution,—this is equal to 23·580 per cent. of chlorine. In a second experiment, other 2000 grs. of the same chloride of lime mixture required 1335 grs. of the fresh-made arsenite solution,—this is equal to 23·669 per cent. of available chlorine.

Mean of the experiments:—

Solution kept 2 months....	23·713 per cent. of chlorine.
The fresh solution.....	23·624 „ „ „

These experiments prove that for all practical purposes an alkaline solution of arsenious acid suffers no change by keeping.

Quantitative Determination of Hippuric Acid by a Volumetric Process. *By* Robert Wreden.

Neutral solutions of alkaline hippurates and perchloride of iron furnish a voluminous fawn-coloured precipitate, which is perfectly insoluble in water, for sulphocyanide of potassium and a drop of nitric acid do not produce the least trace of rose colour in the washing waters. In boiling water this precipitate cakes together into a brown, resinous mass; boiling alcohol, however, dissolves it in large quantity, and, after cooling, tufts of red, oblique rhombic prisms separate from the solution. The precipitate which is thrown down on the addition of solution of perchloride of iron to hippurate of soda, when dried at 212° F. and analysed, gave:—

	Found.		Calculated.
	I.	II.	
$C^{54}\ H^{24}\ N^{3}\ O^{15}$	85·91	86·03	86·441
$Fe^{2}\ O^{3}$	14·09	13·97	13·559

Upon this precipitability of hippuric acid by perchloride of iron the author has founded the following volumetric process. In the first place, care must be taken that all the fluids employed in the process are perfectly neutral, for the slightest excess of acid, even of acetic acid, prevents the reaction. This is also the cause why the determination of phosphoric acid in the urine, which is also effected by means of a solution of chloride of iron, is not rendered incorrect by the simultaneous presence of hippuric acid. Thus during the precipitation of the basic phosphate of iron, free muriatic acid is formed, and this prevents the reaction. In order to detect the completion of the reaction, that is the addition of a small excess

of solution of chloride of iron, a fragment of filtering paper soaked with ferrocyanide of potassium is laid upon a white porcelain plate, and upon this a double piece of filtering paper is pressed with a glass rod to which a drop of the mixture adheres; if an excess of solution of chloride of iron be present, a blue colour is produced in a few seconds.

The normal solution of chloride of iron, of which each cubic centim. must exactly represent 10 milligrms. of hippuric acid ($C^{18} H^9 NO^6$), may be prepared in two ways:—

1. 2·0885 grms. of chemically pure iron are dissolved in pure muriatic acid, and chlorine gas is passed into the mixture until all protochloride is converted into perchloride; the solution is then carefully evaporated to dryness on the water-bath, the residue is dissolved, avoiding the smallest loss, in water, and diluted until it forms 2000 cubic centims. Each cubic centim. of the solution then precipitates 10 milligrms. of hippuric acid ($C^{18} H^9 NO^6$). In any case the solution of perchloride of iron employed, must be free from protochloride and from muriatic acid.

2. The second method is still better. A solution of perchloride of iron of undetermined strength is taken and tested for its value. For this purpose 0·500 grm. of hippuric acid may be neutralized with bicarbonate of soda, and the solution diluted to 250 cubic centims. Every 50 cubic centims. then contain 0·100 grm. of hippuric acid. To 50 cubic centims. of this solution the solution of perchloride of iron is allowed to flow slowly from Mohr's pipette, until a drop of the mixture, tested as above, gives a distinct blue colour. The volume of solution of perchloride of iron used up to this point represents 0·100 grm. of hippuric acid, and it is then very easy to calculate the amount of water necessary to dilute the solution of iron sufficiently to make each cubic centim. represent 0·010 grm. of hippuric acid. It is, however, always best not to add the whole calculated quantity of water at once, but always a little less, so as to be sure of the correctness of the strength by repeated testing with the solution of hippuric acid. This second method is to be preferred to the former, as in it the error caused by the addition of a slight excess of the solution of iron is accounted for in the testing itself, and the degree of blue coloration which indicates the completion of the reaction may also be noticed.

For the determination of hippuric acid in the human urine, the phosphoric acid must first be got rid of. For this purpose the urine is treated with a mixture of 1 vol. of cold saturated solution of nitrate of baryta and 2 vols. of cold saturated solution of caustic baryta. One volume of this mixture is usually quite sufficient to precipitate all the phosphoric, sulphuric, and uric acid from 2 vols. of urine; but if it should appear from the previous determination of phosphoric acid that the ordinary quantity of solution of baryta may not be sufficient, more of it is added, as for example $1\frac{1}{2}$ vol., 2 vols., &c.

For the determination of the hippuric acid, 60 cubic centims. of urine are measured off and mixed with 30 cubic centims. of the solution of baryta; of the filtered fluid 75 cubic centims., repre-

senting 50 cubic centims. of urine, are measured and carefully neutralized with dilute nitric acid. The quantity of hippuric acid in the urine prepared in this manner may now be determined with great accuracy, only it must not be forgotten that after the addition of each half cubic centim. of the solution of iron a drop of the mixture should be tested as above. It is also of importance to observe accurately the intensity of the blue spot produced during the preparation of the normal iron solution, which is likewise the indication of the completion of the reaction. In analyses of urine also the amount of phosphoric acid must always be first determined, for it might happen that the quantity of phosphoric acid was greatly increased; then instead of 30 cubic centims. a larger amount of solution of baryta must be added; for example, 60 cubic centims. of urine would be mixed with 40 cubic centims. of solution of baryta, and of this 83·3 cubic centims. (=50 cubic centims. of urine) would be measured off for the determination of the hippuric acid.

Complete removal of the phosphoric acid and careful neutralization of the alkaline mixture obtained are, therefore, the two conditions upon which the occurrence or non-occurrence of the reaction depends. But as the fulfilment of these conditions presents no great difficulties, it follows that the quantitative determination of the hippuric acid in the urine of healthy and diseased subjects, otherwise so extremely difficult, may now be easily effected by every surgeon, so that a new field of observation in pathological chemistry is opened up.

The author adds a great number of determinations effected by him, from which it appears:—

1. That the solution of baryta precipitates no hippuric acid from the urine, so that it does not render its quantitative determination inaccurate.

2. That the presence of uric acid is not injurious, as it is thrown down by the solution of baryta. Nor can oxalic acid affect the accuracy of the determination of hippuric acid, as it always occurs in the form of oxalate of lime.

3. The error which is caused by the addition of an excess of solution of chloride of iron in order to obtain the terminal reaction with ferrocyanide of potassium, amounts on the average to 10—15 milligrms. of hippuric acid (=1 to $1\frac{1}{2}$ cubic centim. of solution of chloride of iron to 50 cubic centims. of urine). This error cannot be avoided and is very small, if we consider the dilution of the solution of chloride of iron (2·0855 grms. Fe to 2 litres of water, whilst in the determination of phosphoric acid there are 15·566 grms. Fe to 2000 cubic centims. of water), and that the solution is again diluted with 75 cubic centims. of the mixture. From this it appears how important it is to observe the intensity of the blue colour produced at the terminal point of the reaction in the preparation of the normal solution of chloride of iron.

4. From all the experiments hitherto made, it appears that the amount of hippuric acid in the urine is considerably greater than that of phosphoric acid, and not, as supposed by Liebig, equal to that of uric acid. However, the few statements extant of the

amount of hippuric acid in the urine of healthy and diseased human subjects are very inaccurate and different. Thus Bouchardat found 2·23 parts of hippuric acid in 1000 parts of the urine of a patient (=0·223 per cent.); Max Pettenkofer calculated from the alkaline carbonate furnished by the urine of a girl of thirteen years old suffering from Saint Vitus' dance, that 1000 parts of urine contained 12·886 parts of anhydrous hippuric acid (=1·2886 per cent.?). Lastly, Millon reports that he might have obtained 9, 10—11 grms. (=0·91—1·1 per cent.) of hippuric acid from a litre of urine; but as for this purpose he mixed the urine with $\frac{1}{20}$ vol. of concentrated muriatic acid and the crystals of hippuric acid (?) deposited after standing for 24 hours were of a red or brown colour, a good portion of this must be ascribed to uric acid; hippuric acid, on the contrary, is soluble to a considerable extent in free muriatic acid. From 29 determinations of hippuric acid already made by the author in healthy urine, he obtained an average of 0·308 per cent. (min. 0·21 per cent., max. 0·57 per cent.). In the urine of diseased subjects this amount may of course rise considerably, as has already been observed in the urine of fever patients (Lehmann), in chorea (Pettenkofer), in diabetes (Lehmann), &c. The opinion that hippuric acid may be formed independently in the organism, without the aid of the benzoic acid of the food, has already been expressed by Liebig, and may perhaps be confirmed by these numbers.

5. When the phosphoric acid in the urine exceeds 0·160 per cent., that is when more than 8 cubic centims. of the solution of chloride of iron have been employed to 50 cubic centims. of urine, the 60 cubic centims. of urine must be mixed, not with 30 but with 40 cubic centims. of solution of baryta, and 83·3 cubic centims. of the filtered fluid must be measured off, as otherwise one might easily be compelled to repeat the experiment. The author's experiments also show that in the determination of phosphoric acid by Liebig's process it is unnecessary to add 10 cubic centims. of solution of acetate of soda to 50 cubic centims. of urine as a preliminary step; for as hippurate of soda is contained in the urine in greater quantity than phosphoric acid, the muriatic acid set free during the precipitation of the basic phosphate of iron will separate the hippuric acid, and consequently fulfil the office of the acetic acid.

Lastly, it is to be observed that for the determination of hippuric acid, it is absolutely necessary to employ fresh urine, for otherwise we shall have to do with benzoic acid instead of hippuric acid.—*Bull. de St. Pétersb.* xvii. p. 500.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Note on Steinbühl-yellow, a new kind of Chrome-yellow. *By* Dr. L. Pappenheim.

Under the above name a yellow colour has been for some time in commerce which is quite certain to find much favour, although its price is far higher than that of the ordinary chrome-yellow. It is

of a splendid yellow, and differs essentially in its tint from the best samples of chrome-yellow. It is pulverulent, of small specific gravity, loses nothing in weight at a red heat, but becomes transitorily reddish brown, and is partially taken up by water without entirely dissolving in that fluid. It dissolves in muriatic and nitric acids; if the acid is poured over it in a concentrated state, a slight effervescence takes place. When prepared with but little acid the solution is somewhat turbid, but does not leave any considerable portion when filtered. When heated with alcohol, the solution in muriatic acid becomes intensely dark green; if more alcohol and then sulphuric acid be added, a white precipitate is produced. Solution of sulphate of lime does not precipitate the solution of the colour in muriatic acid, but this is done by sulphuric acid with or without the addition of alcohol. The reddish-yellow colour of the solution in nitric acid changes by heating, with the addition of alcohol, into a beautiful blue. If acetate of lead be added to the dilute solution in nitric acid, a heavy precipitate of the colour of chromate of lead makes its appearance. If an excess of lead were added, filtered, the excess of lead and the lime precipitated by sulphuric acid, alcohol added, filtered and evaporated, large quantities gave a residue, which, when dissolved in water and mixed with chloride of platinum with the addition of muriatic acid, furnished octahedra of platinochloride of potassium. The investigation gave no magnesia or other bases except lime and potash. Of acids, besides the chromic acid, which was undoubtedly present from the preceding experiments, there was only a small quantity of sulphuric acid.

When the author mixed a hot saturated solution of bichromate of potash with a saturated solution of chloride of calcium, a precipitate was produced, which, when washed and dried, was undistinguishable from the Steinbühl-yellow.

The substance gave 3·1 per cent. to distilled water after short stirring. With nitrate of silver, the yellow filtrate gave a red precipitate of chromate of silver, which was rapidly converted into white chloride of silver on the addition of a few drops of muriatic acid. Sulphuric acid and alcohol produce a strong turbidity in the filtrate. When boiled with reducing organic matters and muriatic acid, the yellow filtrate loses its colour, without, however, acquiring more than a tinge of green. Acetate of lead precipitates the yellow filtrate, with the colour of chromate of lead. Chloride of platinum produces a very slight turbidity in the original filtrate. Even in 16 hours no precipitate is deposited.

The Steinbühl-yellow consists, therefore, of chromic acid, lime and potash; when stirred for a short time with cold water, it parts with chromate of lime.

The poisonous qualities of chromic acid and its soluble salts, and the circumstance that the colour parts with perceptible, although not large quantities of chromic acid to cold water, render the Steinbühl-yellow an extremely dangerous colouring matter, the employment of which in confectionery and similar trades must not be thought of.—*Monatsblatt des Gewerbe-Vereins zu Köln*, May 1859; *Polytechn. Centralblatt*, 1859, p. 973.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the so-called Cyanoform. By Dr. C. Nachbaur.

A compound of cyanogen, C^2HCy^3, analogous to chloroform, bromoform, and iodoform, is not known with certainty. Nevertheless Bonnet supposed it to exist in the fluid which he obtained by the distillation of acetate of lime with an equal quantity of prussian blue or cyanide of mercury, and of which he states that it contained no acetone, acetic acid, or hydrocyanic acid, but consisted merely of cyanoform and water, the latter of which could be separated by chloride of calcium. He describes cyanoform as a colourless, tolerably volatile, neutral fluid, smelling of hydrocyanic acid and tobacco-smoke, not inflammable, soluble in æther, alcohol, and water. No analysis is given.

A body of this kind appeared to be of great interest, and deserving of more accurate study. The author was induced by Professor Hlasiwetz to undertake the following experiments.

The mixture of cyanide of mercury and dehydrated acetate of lime was distilled over the spirit-lamp at a moderate heat in small portions (about 1 ounce at a time, as the employment of larger quantities gives a smaller result, especially in the most important product of this reaction). A yellowish fluid, which soon becomes brown, and has an empyreumatic odour mixed with an odour of hydrocyanic acid, is obtained; much mercury is reduced; towards the conclusion crystals appear in the neck of the retort, which behave like acetamide; and there remains in the retort a carbonaceous residue. The amount obtained is but small.

This crude product is a rather complicated mixture; it contains acetonitrile, acetone, and hydrocyanic acid; but what Bonnet regards as cyanoform, is a peculiar new base, the description of which will be the principal object of the following observations. It is obtained as follows:—

It is first rectified on the water-bath. For a long time the boiling-point of the fluid remains between 171° and 176° F., and

about half of it passes over perfectly colourless. This is collected by itself. Afterwards the distillation becomes slow, and the bath is removed.

From this time the drops falling are tested from time to time in a watch-glass, by carefully allowing them to flow into a drop of solution of oxalic acid or hydrate of sulphuric acid. When they solidify in a crystalline form under these circumstances, the receiver is to be again changed. The portion now passing over contains the volatile base, which is unfortunately very unstable by itself, but yet furnishes some compounds, which enable one to judge of its nature. This portion has the following properties.

It is colourless, has a peculiar, unpleasant odour, resembling that of propylamine, and possesses an alkaline reaction. In course of time it becomes yellowish. When heated for a long time by itself, or boiled with water, it is decomposed with evolution of hydrocyanic acid. It mixes with water, alcohol, and æther.

With perchloride of platinum a scanty crystalline precipitate is produced. Nitrate of silver gives a precipitate of cyanide of silver, and perchloride of iron a brown precipitate, which, if the proportions were suitable, becomes blue when the fluid is heated. Sulphate of iron produces a yellowish-brown precipitate, which is rendered pulverulent and light green by boiling; if this be treated with cyanide of potassium, perchloride of iron produces the reaction of ferrocyanide of potassium in the filtrate.

When heated with peroxide of mercury, cyanide of mercury is formed; a gas is evolved from the peroxide of mercury, and along with an ammoniacal an ætherial odour is detected. The preparation of this base in a pure state for the purpose of analysis was attempted in vain. Its salts alone can be employed to furnish data for its composition.

Oxalate.—If a concentrated solution of oxalic acid be mixed with the base, care being taken to avoid an excess of the former, the whole immediately sets into an aggregation of dazzlingly white, acicular crystals. The mother-liquor is separated by pressure between linen, the crystals are then washed with ice-cold water, and exposed to such a pressure between paper in a press that they become dry and triturable. This kind of purification must suffice, as they cannot be recrystallized from hot water without decomposition. If their solution be boiled much hydrocyanic acid is evolved, and there remains a solution of oxalate of ammonia. The salt from several preparations, dried under the air-pump, gave on analysis,—

C	46·01	46·53	20=120		46·15
H	7·73	7·47	20	20	7·69
N	21·69	..	4	56	21·54
O	..	..	8	64	24·62

Both the amount of cyanogen and that of oxalic acid contained in the salt were directly determined. To precipitate the former, the solution of the salt, slightly acidulated with nitric acid, was digested for a long time with a solution of silver. The determination of the

oxalic acid was effected by means of an ammoniacal solution of chloride of calcium. The results obtained were,—

$C^{12}H^{18}N^2$	..	..	1=118		45·39
C^4 N^2	20·14	..	1	52	20·00
C^4 H^2 O^8	34·38	34·64	1	90	34·61
$C^{20}H^{20}N^4O^8$					

Sulphate.—The combination of the base with sulphuric acid takes place under the same conditions as with oxalic acid. A crystalline mass is immediately formed, which is treated in the same way as the preceding. It is to be remarked only that a smaller excess of the acid is sufficient to redissolve the whole, for which reason it must be added very carefully, for the salt can no longer be obtained from such a solution. It is also more soluble in water than the oxalate, but it is decomposed like this by boiling. Its analyses gave,—

C	36·15	36·24	16=96		35·82
H	7·50	7·60	20	20	7·46
N	20·61	20·79	4	56	20·89
O	..	..	2	16	5·98
S^2O^6	31·57	31·62	1	80	29·85

The excess of sulphuric acid is probably due to the circumstance that the salt could not be recrystallized. The determination of the cyanogen gave,—

$C^{12}H^{18}N^2$	..	1=118			
C^4 N^2	18·97	1	52		19·40
H^2 O^8S^2	..	1	98		
$C^{10}H^{20}N^4O^8S^2$					

No salts were obtained with *muriatic* and *nitric acids* which could be made use of for analysis. The base, when neutralized with these acids and slowly evaporated, furnished a thickish, deliquescent mass. Succinic acid also does not behave like its homologue, oxalic acid.

Compound with Iodide of Mercury.—The base dissolves periodide of mercury in considerable quantity by the aid of a gentle heat. By this means, especially when the base is used undiluted, more than one compound is obtained.

The principal product of this reaction is obtained in a pure state, when a moderately concentrated solution of the base is saturated with iodide of mercury with the assistance of heat, and the clear fluid is poured away and left to cool. Crystals of the compound are soon formed, which finally cause the whole fluid to solidify. These are silvery laminæ of great beauty, but unfortunately they are not very stable. When exposed to the air they become red. They do not bear heat at all, and even under the air-pump they at least acquire a yellow colour. They dissolve very sparingly in cold water.

The analysis led to the empirical formula $C^{16}H^{18}N^4Hg^8I^4$. It gave,—

C	6·45	16 =	96	6·49
H	1·07	18	18	1·22
N	..	4	56	3·78
Hg	53·41	8	800	54·13
I	33·98	4	508	34·37

A portion of the mercury in this compound is very probably to be assumed as combined with cyanogen.

The described properties and compounds of the base will suffice for its recognition in case of its occurring, or to call it to mind if synthesis should lead to a body of the formula $C^{16}H^{18}N^4$. Until this is the case, we can only advance suppositions as to its constitution. That it contains C^4 and N^2 as cyanogen appears to be beyond doubt. After deducting this there remains $C^{12}H^{18}N^2$, which is the expression for 2 equivs. of trimethylamine.

Perhaps the body belongs to the class of ammoniacal derivatives conjugated with cyanogen, of which Hofmann's cyananiline is a representative, *e. g.*—

$$\left.\begin{matrix}(C^2H^3)^2\\(C^2H^3)^2\\(C^2H^3)^2\end{matrix}\right\}N^2+Cy^2,\text{ and }\left.\begin{matrix}(C^{12}H^5)^2\\H^2\\H^2\end{matrix}\right\}N^2+Cy^2.$$

The agreement in the constitution would be quite complete if we might write

$$C^{16}H^{18}N^4\text{ as }\left.\begin{matrix}(C^6H^7)^2\\H^2\\H^2\end{matrix}\right\}N^2+Cy^2,$$

and refer the body to the propyle series.

It is well known that the salts of cyananiline partake of the decomposability of those above described, and are for the most part incapable of recrystallization.

If gaseous cyanogen be passed into trimethylamine it is rapidly absorbed, becomes heated, and acquires a dark brown colour. In a short time a great quantity of a brown precipitate, similar to paracyanogen, separates. The reaction could only be effected with small quantities, and an attempt was made to obtain the characteristic mercurial salt. When diluted with water and filtered from the brown body, the fluid dissolved iodide of mercury with the aid of heat, and furnished a compound, which to the naked eye appeared very similar to those above described, but under the microscope exhibited forms which were essentially distinct from those of the others.

It is stated above that the more volatile part of the product of distillation of acetate of lime with cyanide of mercury contained acetone and acetonitrile. For the presence of the latter we can only cite reactions; it could not be separated in a pure state.

The volatile mixture, which is at first colourless, becomes brown

after standing for a short time, and lets fall a brown deposit. It has an alkaline reaction. If it be mixed with a concentrated solution of oxalic acid and rectified, an acidulous distillate, with an odour of acetone and hydrocyanic acid, is obtained. The acetonitrile appears to be completely decomposed by this means.

If the distillate be again rectified over carbonate of potash, a fluid passes over possessing all the properties of acetone, and which even forms the well-known double compound with an alkaline bisulphite.

Another portion of the original mixture was washed with dilute solution of potash to combine the hydrocyanic acid, and then after being drawn off and dried, gave the peculiar odour of acetonitrile very decidedly, that of acetone being greatly inferior to it in strength. It burnt with the characteristic flame of cyanogen first observed by Hofmann.

The boiling-points of acetonitrile and acetone are too near to each other to permit the separation being effected by fractional distillation. When the mixture was treated with sulphuric acid in the way adopted by Hofmann and Buckton, in order to convert the acetonitrile into disulphometholic acid, the phænomena corresponding with this reaction certainly did occur, but the baryta salt obtained appeared, from the amount of base which it contained, to be only methylosulphate of baryta.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xxxv. p. 148.

On the Bile of the Kangaroo. By J. Schlossberger.

The author obtained two ounces of the fresh bile of a female kangaroo, which died in Stuttgart of indigestion. It was rendered thickly fluid by mucus, was of a reddish-yellow colour, perfectly neutral, and of a peculiar odour. The bile freed from mucus by alcohol gave the well-known reaction of bile with fuming nitric acid very strikingly, and with sugar and sulphuric acid, the purple colour of the acids of the bile. The analysis gave,—

Water	85·87
Solid matter....	14·13

Mucus with colouring matter	4·34
Cholesterine with fat	1·09
Salts of choleic acid	7·59
Loss and other salts	1·11
	14·13

The purified salts of choleic acid dried at 248° F., the base of which was principally soda, contained 2·47 per cent. of sulphur. The bile of the kangaroo is one of the poorest in taurocholic acid; that of the pig alone is poorer than it of those already investigated. —Liebig's *Annalen*, cx. p. 244.

On the supposed Part played by the so-called Basic Chloride of Calcium in the Manufacture of Chloride of Lime and the Preparation of Caustic Ammonia. *By* Professor Bolley.

The name of basic chloride of calcium is given to the salt obtained by boiling an aqueous solution of chloride of calcium with caustic lime, filtration, and crystallization; it has been investigated especially by H. Rose, and, according to him, has the composition $CaCl + 3CaO + 16HO$. It has frequently been observed in the residue of the preparation of caustic ammonia from muriate of ammonia and slaked lime; and it is of particular importance, that it is also formed in the preparation of pulverulent chloride of lime, in case there is no deficiency of water in the hydrated lime employed. In both operations a part has been ascribed to the occurrence of this salt, namely that it exerts an influence on the amount obtained both of chloride of lime (as regards its amount of effective chlorine) and of ammonia. The author has induced M. Lohner of Thun to ascertain this relation by a series of experiments made in concert with him; their result is here communicated.

It is well known that a given quantity of lime, exposed to a current of chlorine in the form of a thin milk of lime, is capable of taking up nearly twice as much chlorine as burnt lime slaked to powder. On the large scale at least only a solid chloride of lime is obtained, which contains with 1 equiv. of chloride of calcium and 1 equiv. of hypochlorite of lime, about 2 equivs. of caustic lime.

Payen, and with him many chemists, consider the pulverulent chloride of lime as consisting of $4CaO + 2Cl + 4HO$, whilst the fluid contains $2CaO + 2Cl$. The correctness of the opinion that 1 equiv. of dry hydrate of lime can only take up $\frac{1}{2}$ equiv. of chlorine, may remain in abeyance for our purpose. The experiments of Graham corresponding therewith, appear, however, to require revision. The question before us is,—What may be the cause that even when the lime is most finely divided, and the contact with gaseous chlorine is continued as long as possible, nearly half the quantity of the lime remains untouched by the chlorine? The opinion has been expressed that the chloride of calcium formed enters into a combination with the remainder of the lime and water forming the basic chloride of calcium, which hinders the further taking up of chlorine.

In order to test this view, the salt $CaCl + 3CaO + 16HO$ was prepared by boiling a concentrated solution of chloride of calcium with slaked lime, filtering the solution while hot, and leaving it to cool; it was first dried between filtering-paper, then by pressure, and finally under the air-pump, when a few grammes of it were exposed to a current of dry chlorine gas. It soon appeared that the salt contained moisture, as the chlorine taken up displaced water. After dry air free from carbonic acid had been passed through the tube for a short time in order to remove any mechanically adherent chlorine, the tube was emptied, and its contents tested volumetrically for effective chlorine. An amount of $9\frac{1}{2}$ per cent. of chlorine was found. As this amount of chlorine did not represent the com-

plete conversion of the CaO present into CaCl + CaO, ClO, the salt was freed from water by pressure between bibulous paper, and again exposed to the stream of chlorine. A second sample tested in the same way, showed an amount of chlorine of 12 per cent. The salt had again become very moist, although the chlorine gas had been completely dried. The attempt to increase the quantity of chlorine in the salt was given up, as it was sufficiently proved by the above experiments that basic chloride of calcium is not capable of resisting the action of chlorine. The obstacle to dry chloride of lime, prepared on a large scale, acquiring the full possible amount of chlorine is therefore probably for the most part of mechanical nature, but may also be due to chemical impurities in the lime.

With regard to the part played by basic chloride of calcium in the preparation of caustic ammonia, Mohr has treated in detail in his 'Commentary on the Prussian Pharmacopœia,' under the article *Liquor ammonii caustici*. He describes the quantities of water and lime which are best adapted for producing the complete decomposition of the muriate of ammonia. With regard to the water, it is certainly quite true that two phænomena depend upon its quantity, namely that of the overflow of the mixture at a certain thickness, and the passing over of aqueous vapour with the ammoniacal gas, by which the receiver is heated.

Mohr also says, "The formation of this salt (basic chloride of calcium) is the reason why in the presence of much water the muriate of ammonia is not decomposed by an excess of lime, as the latter enters into combination with the chloride of calcium. At a higher temperature, and when there is a loss of water, a mutual reaction again takes place, and ammonia is again evolved in proportion as the water is driven off:" and further, "From these causes it follows most distinctly, that basic chloride of calcium may be contained together with muriate of ammonia in a dilute fluid, without these two bodies being decomposed by mere boiling; but that the action recommences with the loss of water, and the desiccation of the mixture and the elevation of temperature thereby produced," &c.

We have first of all to ascertain accurately how these positions are to be understood. Basic chloride of calcium contains to 55·5 parts of chloride of calcium, 84 parts of lime (CaO) and 144 parts of water; but it is only formed on the cooling of a hot, perfectly saturated solution of chloride of calcium which has been boiled with hydrate of lime. If we assume the existence of the salt in the solution, Mohr's meaning would have to be interpreted as follows,—that in a solution in which there are the above proportions of water, chloride of calcium and lime, there may be an excess of muriate of ammonia, which is decomposed by lime with more difficulty than with a larger or smaller quantity of water. This opinion is evidently improbable; and the affair becomes still more indistinct by the statement "that basic chloride of calcium may be contained together with muriate of ammonia in a dilute fluid, without these two bodies decomposing each other by mere boiling." Crystallized

"basic chloride of calcium" was mixed with powdered muriate of ammonia, and a strong odour of ammonia was evolved, even at the ordinary temperature.

A mixture of powdered muriate of ammonia with crystallized chloride of calcium in the proportion of 1 part of the former to 3 parts of the latter was heated in a flask, and the vapours evolved collected by condensation. The amount of ammonia in the fluid corresponded within a very little with that of the muriate of ammonia employed. 1 part of muriate of ammonia was mixed with 2 parts of crystallized basic chloride of calcium and 2 parts of water in a flask, and boiled for some time. The vapours evolved were carefully collected in a normal solution of oxalic acid, and the ammonia passing over was thus determined. The quantity obtained corresponded with 80 per cent. of the lime contained in the basic chloride of calcium, that is to say, 80 per cent. of the lime contained in this salt served for the decomposition of the muriate of ammonia, under the supposition that 1 equiv. of lime decomposes 1 equiv. of muriate of ammonia. 88 per cent. of the lime present would have been necessary to decompose the whole of the muriate of ammonia. In this case the boiling was not continued long enough. Another experiment, in which muriate of ammonia, basic chloride of calcium, and water were mixed in the same proportions, showed that when the mixture had been longer boiled, there was no muriate of ammonia in the residue.

From these experiments it follows undoubtedly that the salt $CaCl+3CaO+16HO$ cannot present any obstacle to the decomposition of muriate of ammonia, either by itself or when mixed with water (when, moreover, it is again decomposed).—*Schweiz. Polyt. Zeitschrift*, 1859, p. 54; *Polytechn. Centralblatt*, 1859, p. 964.

On Lead-poisoning with Snuff. *By* W. Wicke.

To the cases of lead-poisoning with snuff which have lately been made known, Dr. Alfter has just added a new one in Nos. 10 and 11 of the 'Medicinische Zeitung,' published by the Medical Society of Prussia. We may here pass over the morbid phænomena produced. The violent attacks of colic experienced by the patient first awakened the suspicion that it was a case of poisoning by lead. However, no source could be found for the poison except the snuff which the patient consumed in large quantities. He had constantly taken the same kind for seven years. Höckel examined the snuff, and found that it contained $2\frac{1}{2}$ per cent. of lead. He supposes that a lead-liquor had probably been added to the snuff.

The author has always found that the snuff which is packed in lead-foil contains lead. The longer it has been kept the greater is the amount of lead. Samples sent in bottles or jars always proved free of lead, or contained that metal only in such small quantities as could not be determined by weighing.

The ordinary samples of snuff are firmly pressed, longish quadrangular cakes, which are first wrapped in lead-foil and then in a

double envelope of paper. The outer covering is usually thick blue paper; the inner one finer, and often of a yellow colour. On opening one of these packets the inner paper is usually found to be very damp, the lead superficially oxidized, but in many places much corroded. These spots especially have a crust of a whitish salt. The paper also, even the outer blue coat now and then, exhibits white chalk-like points. Lastly, the cake, especially when dried, appears to be covered with a white granular saline coat, somewhat resembling mould. This white substance is in all cases carbonate of lead.

Keeping snuff in damp places, especially in cellars, must contribute greatly to its becoming poisonous. The samples examined by the author still contained more than 42 per cent. of moisture. Tobacco, as a humous substance, is a source of carbonic acid, without taking into consideration the fact that the air in cellars may itself be richer than ordinary in carbonic acid. The carbonate of lead produced is carried into the cake itself by the moisture. That this is the course taken by the salt is shown by the observation, that the cake contains less lead the further we go from the surface.

Analysis gave for the inner mass 0·951 per cent. of carbonate of lead, for the outer crust 2·743 per cent.; whilst the paper which had been in immediate contact with the lead-foil gave 1·638 per cent.

The lead-foil is certainly tinned on one side. But this is an insufficient protection; and it becomes a perfectly superfluous precaution, when, as was repeatedly observed by Wicke, the tin coat has been turned outwards by the carelessness of the packers. But even when this is not the case, the tin is eaten through, and a free communication between all parts is set up. That the mischief is produced by packing in lead also appears from the fact, that at the edges of the cake, where the contact with the envelope was most complete, the deposit of carbonate of lead was also the greatest.

In poisoning with snuff containing lead absorption may possibly assist, but Wicke regards it as more probable that it takes place principally from the stomach. It is well known that in snuff-takers the pharynx is very often coated with snuff. Thus small quantities of carbonate of lead will be constantly reaching the stomach. At the same time the mode of taking snuff, the greater or less force with which the pinch is drawn up, may also have some influence.—*Zeitschrift für rationelle Medicin*, 1859.

On Cyanide of Mercury and Acetonitrile. *By* O. Hesse.

By bringing in contact cyanide of mercury and acetonitrile (cyanide of methyle), the author obtained a crystalline mass, in which, after it had stood for some months, rectangular laminæ were to be recognized. The crystals crackle when rubbed with a glass rod; on exposure to the air, they lose their peculiar glassy lustre, and fall to a white powder, with evolution of cyanide of methyle. The constitution of this compound appears to be expressed by the formula $C^4 H^3 N, 4HgCy$.—Liebig's *Annalen*, cx. p. 202.

On the Fibroine of Spider's Threads (Sericine). *By* J. Schlossberger.

From the author's experiments it appears that the substance of spider's threads behaves like that of silk. Both dissolve in ammoniacal solutions of protoperoxide of nickel and peroxide of copper. The spider's threads disappear so rapidly in these fluids that they are not observed to swell up.

The fibroine of the common sponge is insoluble in the above fluids, as the author has already proved, and it therefore appears advisable to adopt the name of *sericine* for the substance of silk and spider's threads.—Liebig's *Annalen*, cx. p. 245.

Cleaning Glasses and Capsules. *By* C. Brunner.

There is often a difficulty in cleaning glasses or porcelain capsules to which organic matters have adhered, and in course of time become so hard and dry that they resist all solvents. The following process will be found to answer in almost every case:—

The spots to be cleaned are moistened with concentrated sulphuric acid, and powdered bichromate of potash is sprinkled upon the acid; the objects are then left standing for some hours (through the night) in a moderately warm place. All organic matters are by this means destroyed, with formation of sulphate of chromium, which may be removed by water with the residue of the acid.—Dingler's *Polytechn. Journal*, cl. p. 378.

ANALYTICAL CHEMISTRY.

On the Estimation of Tannine in some Tanning Materials. *By* John Mulligan *and* John Dowling, *Students in the Evening Class for Practical Chemistry, Museum of Irish Industry**.

The following estimations of tannine in some tanning materials were made by precipitating the tannine by means of a standard solution of gelatine containing a small quantity of alum. The alum effects a more complete separation of the tannate of gelatine, and was first recommended for this purpose by Gustav Müller. The solution of gelatine was made by adding to about 9000 grs. of boiling distilled water 30 grs. of the finest isinglass, and afterwards boiling the liquid for 5 or 10 minutes; the solution was then allowed to cool, and when cold 10 grs. of alum were added, and the solution was made, by the addition of distilled water, to measure exactly 10,000 grs. The amount of tannine a given volume of it would precipitate, was ascertained by determining what quantity was required to precipitate a quantity of absolutely pure tannine which had been weighed very accurately.

The gelatine solution was not kept more than 2 days, and the

* Communicated by the Authors; having been read at the Meeting of the British Association at Aberdeen, September 14, 1859.

strength of each fresh solution was always determined in the way just stated.

The tannine was dissolved out of the tanning materials in the following way:—a weighed quantity was allowed to digest 7 or 8 hours in 4000 grs. of cold distilled water, the solution was then decanted, and the tanning material was again digested in about 2000 grs. more of cold distilled water for 3 or 4 hours; after decanting this solution, the material was washed with cold distilled water; the washings were added to the two previous solutions, and the whole made up to a given volume. Two measured portions of the infusion were then taken, and in each portion the tannine was determined. The residue of the tanning material was then digested in distilled water for 24 hours; after the expiration of that time, if the liquid contained any tannine, it was determined by means of the gelatine solution. In order to effect the exact precipitation of the tannine, it is necessary, when it is nearly all precipitated, to filter a portion of the infusion after the addition of the gelatine solution, and test the filtrate for tannine by means of a few drops of the standard gelatine solution. We found Mr. Warington's plan of filtering through a piece of sponge placed in a glass tube to be the most convenient; but instead of filtering upwards, as Mr. Warington recommended, we found that if it was filtered downwards the filtration proceeded much more rapidly, and the filtrate was brighter.

The investigation was conducted in the laboratory of the Museum of Irish Industry, under the direction of Mr. Galloway.

British Oak Bark (age 50 years).—Infused 100 grs. in cold water for 24 hours, and made up the infusion, in the way previously described, to 8000 grs.

I. 2000 grs. of the infusion required 640 grs. of a standard solution of gelatine (1543 grs. of gelatine solution=5 grs. of tannine) to precipitate the tannine=2·07 grs. of tannine=8·28 per cent. of tannine.

II. Other 2000 grs. of the infusion required 660 grs. of the same gelatine solution=2·14 grs. of tannine=8·56 per cent.

The infusion of the residue required 150 grs. of the same gelatine solution=0·48 per cent. of tannine.

The following is the quantity of tannine in 100 parts of the oak bark:—

Analyses.		Mean.		Residue.		Total amount.
I.	II.					
8·28	8·56	8·42	+	0·48	=	8·90

Two other analyses made with a fresh solution of the bark and a fresh gelatine solution, gave the following numbers:—

Analyses.		Mean.	Residue.	Total amount.
I.	II.			
8·55	8·17	8·36	0·56	8·92

British Oak Bark (age about 50 years).—Infused 100 grs. of the bark in cold water for 24 hours, and made up the infusion to 8000 grs.

I. 2000 grs. of the infusion required 650 grs. of a standard solution of gelatine (1615 grs. of gelatine solution=5 grs. of tannine) to precipitate the tannine=2·01 of tannine=8·04 per cent.

II. 2000 grs. of the infusion required 670 grs. of same gelatine solution=2·074 grs. of tannine=8·29 per cent.

The infusion of the residue required 520 grs. of the same gelatine solution=1·60 per cent. of tannine.

The following is the quantity of tannine in 100 parts of the bark:—

Analyses.		Mean.		Residue.		Total amount.
I.	II.					
8·04	8·29	8·16	+	1·60	=	9·76

British Oak (age about 70 years).—Infused 100 grs. of this bark in cold water, and made up the infusion to 8000 grs.

I. 3000 grs. of the infusion required 650 grs. of the standard solution of gelatine (1536 grs. of the gelatine solution=5 grs. tannine) to precipitate the tannine=2·11 grs. of tannine=5·63 per cent.

II. Other 3000 grs. of the infusion required 600 grs. of the same gelatine solution=1·95 gr. of tannine=5·21 per cent.

The infusion of the residue required 220 grs. of the standard solution of gelatine (1568 grs. of the gelatine solution=5 grs. tannine) =0·70 per cent. of tannine.

The following is the quantity of tannine in 100 parts of the bark:—

Analyses.		Mean.		Residue.		Total amount.
I.	II.					
5·63	5·21	5·42	+	0·70	=	6·12

Southampton Oak Bark (age 50 years).—Infused 100 grs. of this bark in cold water, and made up the infusion to 7000 grs.

I. 2000 grs. of the infusion required 730 grs. of a standard solution of gelatine (1628 grs. gelatine solution=5 grs. tannine) to precipitate the tannine=2·24 grs. tannine=7·84 per cent.

II. Other 2000 grs. of the infusion required 705 grs. of the same gelatine solution=2·16 grs. tannine=7·56 per cent.

The infusion of the residue required 400 grs. of a standard solution of gelatine (1560 grs. of gelatine solution=5 grs. tannine) =1·28 per cent. of tannine.

Infused a second 100 grs. of same bark in cold water, andmade up the infusion to 9000 grs.

III. 2000 grs. of the infusion required 620 grs. of a standard solution of gelatine (1835 grs. gelatine solution=5 grs. tannine) to precipitate the tannine=1·69 gr. tannine =7·63 per cent.

IV. A second 2000 grs. of the infusion required 610 grs. of the same gelatine solution=1·66 gr. tannine=7·47 per cent.

The infusion of the residue required 400 grs. of the same gelatine solution=1·09 per cent. of tannine.

The following is the quantity of tannine in 100 parts of the bark :—

Analyses. I.	Analyses. II.	Mean.		Residue.		Total amount.
7·84	7·56	7·70	+	1·28	=	8·98
III.	IV.					
7·60	7·47	7·53	+	1·09	=	8·62

British Coppice Oak Bark (picked sample).—Infused 100 grs. of this bark, and made up the infusion to 9000 grs.

I. 3000 grs. of this infusion required 1210 grs. of a standard solution of gelatine (1536 grs. of gelatine solution=5 grs. tannine) to precipitate the tannine=3·94 grs. tannine=11·82 per cent.

II. Other 3000 grs. of the infusion required 1200 grs. of the same solution of gelatine=3·90 grs. tannine=11·70 per cent.

The infusion of the residue required 180 grs. of the same gelatine solution=0·58 per cent. of tannine.

Infused a second 100 grs. of the same bark in cold water, and made up the infusion to 9000 grs.

III. 2000 grs. of this infusion required 760 grs. of a standard solution of gelatine (1514 grs. of gelatine solution=5 grs. tannine) to precipitate the tannine=2·5 grs. tannine=11·29 per cent.

IV. 2000 grs. of this infusion required 780 grs. of the gelatine solution=2·57 grs. tannine=11·56 per cent.

The infusion of the residue required 300 grs. of a standard solution of gelatine (1568 grs. of gelatine solution=5 grs. tannine) to precipitate the tannine=0·95 per cent. of tannine.

The following is the quantity of tannine in 100 parts of this bark :—

Analyses. I.	Analyses. II.	Mean.		Residue.		Total amount.
11·82	11·70	11·76	+	0·58	=	12·34
III.	IV.					
11·29	11·56	11·42	+	0·95	=	12·37

Irish Oak Bark (picked sample; age about 45 years).—Infused 100 grs. in cold water, and made up the infusion to 8000 grs.

I. 2000 grs. of the infusion required 830 grs. of a standard solution of gelatine (1844 grs. of the gelatine solution=5 grs. of tannine) to precipitate the tannine=2·25 grs. tannine=9·00 per cent.

II. 2000 grs. of the infusion required 810 grs. of the same solution of gelatine=2·20 grs. tannine=8·80 per cent.

The infusion of the residue required 220 grs. of the same gelatine solution=0·60 per cent. of tannine.

The following is the quantity of tannine in 100 parts of this bark :—

Analyses.						
I.	II.	Mean.		Residue.		Total amount.
9·00	8·80	8·90	+	0·60	=	9·50

Belgian Oak Bark (Popering or Plantzen).—Infused 100 grs. of this bark in cold water, and made up the infusion to 7000 grs.

I. 2000 grs. of the infusion required 700 grs. of a standard solution of gelatine (1560 grs. gelatine solution=5 grs. tannine) to precipitate the tannine=2·24 grs. tannine=7·84 per cent.

II. Other 2000 grs. of the infusion required 650 grs. of the same gelatine solution=2·08 grs. tannine=7·28 per cent.

The infusion of the residue required 240 grs. of the same gelatine solution=0·77 per cent. of tannine.

The following is the quantity of tannine in 100 parts of this bark:—

Analyses.						
I.	II.	Mean.		Residue.		Total amount.
7·84	7·28	7·56	+	0·77	=	8·33

Belgian heavy Coppice Oak Bark (picked sample).—Infused 100 grs. of this bark in cold water, and made the infusion up to 9000 grs.

I. 2000 grs. of this infusion required 680 grs. of a standard solution of gelatine (1560 grs. gelatine=5 grs. tannine) to precipitate the tannine=2·18 grs. tannine=9·81 per cent.

II. Other 2000 grs. of the infusion required 670 grs. of the same gelatine solution=2·14 grs. tannine=9·63 per cent.

The infusion of the residue required 320 grs. of the same gelatine solution=1·02 per cent. of tannine.

The following is the quantity of tannine in 100 parts of this bark:—

Analyses.						
I.	II.	Mean.		Residue.		Total amount.
9·81	9·63	9·72	+	1·02	=	10·74

Belgian light Coppice Oak Bark (picked sample).—Infused 100 grs. of this bark in cold water, and made up the infusion to 8000 grs.

I. 2000 grs. of the infusion required 610 grs. of a standard solution of gelatine (1560 grs. gelatine solution=5 grs. tannine) to precipitate the tannine=1·94 gr. tannine=7·76 per cent.

II. Other 2000 grs. of the infusion required 600 grs. of the same gelatine solution=1·92 gr. of tannine=7·68 per cent.

The infusion of the residue required 250 grs. of the same gelatine solution=0·80 per cent. of tannine.

The following is the amount of tannine in 100 parts of this bark:—

Analyses.						
I.	II.	Mean.		Residue.		Total amount.
7·76	7·68	7·72	+	0·80	=	8·52

Cork-tree Bark.—Infused 100 grs. of this bark in cold water, and made up the infusion to 8000 grs.

I. 2000 grs. of the infusion required 817 grs. of a standard solution of gelatine (1368 grs. gelatine solution=5 grs. tannine) to precipitate the tannine=2·98 grs. tannine=11·92 per cent.

II. Other 2000 grs. of the infusion required 800 grs. of the same gelatine solution=2·92 grs. tannine=11·68 per cent.

The infusion of the residue required 100 grs. of the same gelatine solution=0·36 per cent. of tannine.

The following is the quantity of tannine in 100 parts of this bark :—

Analyses.		Mean.		Residue.		Total amount.
I.	II.					
11·92	11·68	11·80	+	0·36	=	12·16

Mimosa Bark.—Infused 100 parts of this bark in cold water, and made up the solution to 10,000 grs.

I. 3000 grs. of the infusion required 1450 grs. of a standard solution of gelatine (1418 grs. of gelatine solution=5 grs. tannine) to precipitate the tannine=5·11 grs. tannine=17·09 per cent.

II. Other 3000 grs. of this infusion required 1450 grs. of the same gelatine solution=5·11 grs. tannine=17·09 per cent.

The infusion of the residue required 250 grs. of the same gelatine solution=0·88 per cent. of tannine.

The following is the quantity of bark in 100 parts of this bark :—

Analyses.		Mean.		Residue.		Total amount.
I.	II.					
17·09	17·09	17·09	+	0·88	=	17·97

Willow Bark.—Infused 100 grs. of this bark in cold water, and made up the infusion to 9000 grs.

I. 2000 grs. of the infusion required 285 grs. of a standard solution of gelatine (1884 grs. of gelatine solution=5 grs. tannine) to precipitate the tannine=0·75 gr. tannine=3·37 per cent.

II. Other 2000 grs. of infusion required 300 grs. of the same solution of gelatine=0·80 gr. tannine=3·64 per cent.

The infusion of the residue required 170 grs. of the same gelatine solution=0·45 per cent. of tannine.

The following is the amount of tannine in 100 parts of this bark :—

Analyses.		Mean.		Residue.		Total amount.
I.	II.					
3·37	3·64	3·50	+	0·45	=	3·95

Larch Bark.—Infused 100 grs. of this bark in cold water, and made up the infusion to 6000 grs.

I. 2000 grs. of this infusion required 310 grs. of a standard solution of gelatine (1568 grs. gelatine solution=5 grs. tannine) to precipitate the tannine=0·99 gr. tannine=2·97 per cent.

The infusion of the residue required 170 grs. of the same solution of gelatine=0·54 gr. of tannine.

The following is the amount of tannine in 100 parts of this bark:—

Mean.		Residue.		Total amount.
2·97	+	0·54	=	3·51

Hemlock Bark.—Infused 50 grs. of this bark in cold water, and made up the infusion to 8000 grs.

I. 2000 grs. of this infusion required 660 grs. of a standard solution of gelatine (1844 grs. gelatine solution=5 grs. tannine) to precipitate the tannine=1·79 gr. tannine=14·32 per cent.

II. Other 2000 grs. of the infusion required 620 grs. of a standard solution of gelatine (1833 grs. gelatine solution=5 grs. tannine) to precipitate the tannine=1·69 gr. tannine=13·52 per cent.

The following are the results in 100 parts:—

Analyses.		Mean.
I.	II.	
14·32	13·52	13·92

Divi-Divi.—Infused 100 grs. in cold water, and made up the infusion to 8000 grs.

I. 2000 grs. of the infusion required 2300 grs. of a standard solution of gelatine (1543 grs. of gelatine solution=5 grs. tannine) to precipitate the tannine=7·45 grs. tannine=29·80 per cent.

II. Other 2000 grs. of this infusion required 2300 grs. of the same gelatine solution=7·45 grs. tannine=29·80 per cent.

The following are the results in 100 parts:—

Analyses.		Mean.
I.	II.	
29·80	29·80	29·80

Valonia (*Smyrna*).—Infused 50 grs. of it in cold water, and made up the infusion to 8000 grs.

I. 2000 grs. of the infusion required 1250 grs. of a standard solution of gelatine (1560 grs. gelatine solution=5 grs. tannine) to precipitate the tannine=4·00 grs. tannine=32·00 per cent.

II. Other 2000 grs. of the infusion required 1310 grs. of the gelatine solution=4·2 grs. tannine=33·60 per cent.

The residue required 310 grs. of the same gelatine solution=0·99 gr. tannine=1·98 per cent.

The following is the quantity of bark contained in 100 parts of this bark:—

Analyses.		Mean.		Residue.		Total amount.
I.	II.					
32·00	33·60	32·80	+	1·98	=	34·78

Myrabolams.—Infused 100 grs. in cold water, and made up the infusion to 7000 grs.

I. 2000 grs. of the infusion required 1700 grs. of a standard solution of gelatine (1441 grs. of gelatine solution=5 grs. tannine) to precipitate the tannine=5·90 grs. tannine=20·65 per cent.

II. Other 2000 grs. of the infusion required 1560 grs. of the same gelatine solution=5·41 grs. tannine=18·93 per cent.

The infusion of the residue required 325 grs. of the same gelatine solution=1·12 per cent.

The following is the amount of tannine in 100 parts of this substance:—

Analyses.		Mean.		Residue.		Total amount.
I.	II.					
20·65	18·93	19·79	+	1·12	=	20·91

Palermo Shumac.—Infused 50 grs. of this in cold water, and made up the infusion to 9000 grs.

I. 2000 grs. of the infusion required 650 grs. of a standard solution of gelatine (1410 grs. gelatine solution=5 grs. tannine) to precipitate the tannine=2·30 grs. tannine=20·70 per cent.

II. 2000 grs. of the infusion required 670 gas. of the same gelatine solution=2·37 grs. tannine=21·33 per cent.

The infusion of residue required 475 grs. of the same gelatine solution=1·68 gr. tannine=3·36 per cent.

The following is the quantity of tannine contained in 100 parts:—

Analyses.		Mean.		Residue.		Total amount.
I.	II.					
20·70	21·33	21·01	+	3·36	=	24·37

Bombay Catechu (light brown colour).—Infused 50 grs. of this in cold water, and made up the infusion to 8000 grs.

I. 2000 grs. of the infusion required 900 grs. of a standard solution of gelatine (1410 grs. gelatine solution=5 grs. tannine) to precipitate the tannine=3·19 grs. tannine=25·52 per cent.

II. Other 2000 grs. of the infusion required 930 grs. of the same gelatine solution=3·30 grs. tannine=26·40 per cent.

The infusion of the residue required 52 grs. of the same solution of gelatine=0·18 gr. tannine=0·36 per cent.

The following is the amount of tannine contained in 100 parts:—

Analyses.		Mean.		Residue.		Total amount.
I.	II.					
25·52	26·40	25·96	+	0·36	=	26·32

Pegu Catechu (colour dark brown).—Infused 50 grs. in cold water, and made up the infusion to 8000 grs.

I. 2000 grs. of the infusion required 1525 grs. of a standard solution of gelatine (1441 grs. of gelatine solution=5 grs. tannine) to precipitate the tannine=5·29 grs. tannine=42·32 per cent.

II. Other 2000 grs. of the infusion required 1540 grs. of the same gelatine solution=5·34 grs. tannine=42·72 per cent.

The infusion of the residue required 630 grs. of the same gelatine solution = 2·18 grs. tannine = 4·36 per cent.

The following is the amount of tannine in 100 parts :—

Analyses.		Mean.		Residue.		Total amount.
I.	II.					
42·32	42·72	42·52	+	4·36	=	46·88

The following Table contains the average amount of tannine found by different chemists in the tanning materials we have examined :—

	Per cent.	Authority.
Oak bark formation, 100 years old	8·45	C. Müller.
„ „ young	13·87	„ „
„ „ British, 50 years old	8·90	Mulligan & Dowling.
„ „ „ age about 50 years	9·76	„ „
„ „ „ „ „ 70 „	6·12	„ „
„ „ Southampton, age about 50 years	8·80	„ „
„ „ Coppice, picked sample	12·35	„ „
„ „ Irish, picked sample, age 45 years	9·50	„ „
Oak, old, white inner bark	21·00	Cadet de Gassincourt.
„ „ „ „ „	14 20	Davy.
„ young, „ „	15·20	„
„ „ coloured or middle bark	4·00	„
„ „ entire bark	6·00	Davy & Geiger.
„ „ spring-cut bark	22·00	Davy.
Oak bark, Belgian Popering	8·33	Mulligan & Dowling.
„ „ „ heavy Coppice, picked sample	10·74	„ „
„ „ „ light	8·52	„ „
„ „ Eschurg	19·35	G. Müller.
Mimosa bark	17·97	Mulligan & Dowling.
„ „	31·16	G. Müller.
Willow bark	3·95	Mulligan & Dowling.
Willow, Leicester, white inner bark	16·00	Davy.
„ „ coloured or middle bark	3·10	„
„ „ entire bark	6·80	„
„ Weeping	16·40	Cadet de Gassincourt.
Larch bark	3·51	Mulligan & Dowling.
„ „	1·60	Davy.
Cork-tree bark	12·16	Mulligan & Dowling.
Hemlock bark	13·92	„ „
Divi-Divi	29·80	„ „
„ „	49·25	G. Müller.
Valonia, Smyrna	34·78	Mulligan & Dowling.
Myrabolams	20·91	„ „
Shumac	19·35	G. Müller.
„ Palermo	24·37	Mulligan & Dowling.
„ „	16·20	Davy.
„ Malaga	10·40	Frank.
„ Carolina	5·0	Cadet de Gassincourt.
„ Virginian	10·00	„ „
Catechu, Bombay, light colour	26·32	Mulligan & Dowling.
„ „ „ „	55·00	Davy.
„ Pegu, dark brown colour	46·88	Mulligan & Dowling.
„ Bengal	44·00	Davy.

The advantage of adding alum to the gelatine solution is most appreciated on the determination of tannine in the bark-liquors of tanneries; without the addition of alum it is impossible, we have found, to make even an approximative estimation of the tannine in these solutions. Müller, to whom the merit is due of first proposing the addition of alum, does not appear to have tried the gelatine solution with alum on tanner's liquors.

On the Detection of small Quantities of Arsenic and Iodine by means of the Iodine Galvanometer. *By* M. Osann.

For the detection of small quantities of bodies by a galvanic process, the arrangement described by the author in several previous memoirs is peculiarly adapted. He gave it the name of the iodine-galvanometer, because he formerly employed it principally to detect weak currents by the decomposition of iodide of starch. This apparatus acts through two platinum wires, which are fastened into a support, and the two bent ends (*a a*) of which terminate in little cups of glass for the reception of mercury. The other two ends (*b b*) of these platinum wires, which are directed downwards, are placed above a watch-glass, upon which starch-paste, moistened with iodide of potassium, may be laid when it is desired to detect a weak current by the reaction of iodine and starch. The two platinum wires may be removed from each other to any desired distance by means of a screw. This apparatus may of course be employed for all operations in which delicate galvanic decompositions are to be effected. To enable these to be observed more readily, a lens is attached on the right-hand side of the stage which bears the watch-glass in a hole or cavity; this is arranged so that it may be moved to and fro. This apparatus may also be very well employed in detecting the action of statical electricity upon chemical compounds. For this purpose a copper wire is immersed in one of the mercurial cups, receiving one of the ends (*a a*) of the platinum wires, and the free pointed end of the copper wire is turned towards the conductor of an electrical machine. A second copper wire is inserted into the other mercurial cup, whilst its free end touches the floor and serves to conduct the electricity away. Iodide of potassium is immediately decomposed.

A mixture of 1 part by weight of sulphuric acid and 6 parts by weight of water is put into a platinum crucible, the opening of which is closed by a card-board cover, holding an amalgamated zinc rod, and the ends (*a a*) of the platinum wires are united with conducting wires, of which one proceeds from the zinc rod and the other from the crucible. A watch-glass filled with commercial muriatic acid is now placed upon the stage, and screwed up until the two platinum wires dip into it. If the two wires be observed, a distinct evolution of hydrogen gas will be perceived at the negative pole. No evolution of chlorine is detected at the positive pole, because this is partly absorbed by the fluid and partly employed in dissolving the platinum.

Small quantities of arsenic and iodine are detected by Osann with his apparatus in the following way:—

1. 0·0160 grm. of arsenious acid in fragments were weighed, put into a mortar and pounded. A corresponding quantity of dilute, warm muriatic acid was then poured to it, and left in contact with it until the arsenious acid was dissolved. Aqueous hydrosulphuric acid added to this fluid, gave a very perceptible reaction of yellow sulphuret of arsenic. It was then diluted with water, until a sample of it no longer showed any reaction with the above fluid. A watch-glass of $1\frac{3}{4}$ inch in diameter was now filled with it and exposed to the action of Osann's small coke battery in the iodine-galvanometer. A dark coating of metallic arsenic was soon perceptible at the negative pole. A small watch-glass of half the diameter of the preceding was then filled with water containing one or two drops of muriatic acid; the poles were changed so that the former cathode became the anode, and the stage was then screwed up so that the ends of the platinum wires dipped under the surface of the fluid. The metallic coating instantly disappeared. When aqueous hydrothionic acid was added to this fluid, a yellowish-white turbidity of sulphuret of arsenic was produced.

2. 0·0086 grm. of iodide of potassium were dissolved in 40 grms. of water. Two drops of this solution were put into a small watch-glass, and starch-paste was added. The addition of a drop of fuming nitric acid immediately produced a strong violet reaction. 60 grms. of water were then added. When tested again as before a reaction took place, but this was weaker. The fluid was again mixed with 100 grms. of water; the reaction was very weak. 50 grms. more water were added. At the first moment, when the vapours of hyponitric acid came in contact with it, a slight greenish colour was produced, but this immediately diappeared. Of this fluid 100 grms. were poured off and mixed with 200 grms. of water. The fluid exhibited no reaction which could indicate iodine. The watch-glass was then filled with this fluid and exposed in the iodine-galvanometer to the action of a coke battery. A blue cloud very soon made its appearance at the anode. The effect is particularly distinct when the stage on which the watch-glass is supported is screwed down. A violet spot is then seen at the point which was in contact with the platinum wire.—*Verhandl. der Würzburg. Phys.-med. Gesellsch.*, 1859.

On the Applicability of Molybdate of Ammonia to the Detection of Phosphoric Acid. By G. Städeler.

The author calls attention to the fact that a solution of perchloride of iron, diluted with water until it is entirely deprived of colour, acquires a bright yellow colour when mixed with muriatic acid. Nitrate of iron behaves in the same way. If therefore a solution containing iron be tested with molybdate of ammonia, this circumstance may easily lead to a mistake, in consequence of which phosphoric acid may be supposed to exist where it is not in reality present.—Liebig's *Annalen*, cix. p. 313.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On a new Mode of Decomposition of Trinitrophenylic Acid.

By H. HLASIWETZ.

THE author has made some experiments with the view of effecting the reduction of highly nitrited bodies by means of cyanogen.

If a solution of picric acid be mixed with one of cyanide of potassium, both concentrated and hot, the fluid immediately acquires a blood-red colour and becomes filled with fine dark-red crystals, which cause it to set into the form of a jelly on cooling. According to numerous observations, the best proportions of the substances to be employed are:—

2 parts of cyanide of potassium (prepared by Liebig's method) dissolved in 4 parts of water, and 1 part of picric acid in 9 parts of water; the hot solution of the latter is to be poured into the first fluid, heated to 140° F., and constantly stirred.

The mass smells strongly of ammonia and hydrocyanic acid, and on cooling forms a soft crystalline paste. In the course of a few hours it is strained through linen, and then strongly pressed in paper. The reddish-brown bronze-like crude crystalline mass is then triturated with a little water, heated in a dish, put upon a filter and washed with cold water; it is then again pressed, dissolved in a large quantity of boiling water in a flask, filtered through a warm filter and left to crystallize.

The deep purple filtrate soon becomes covered with a metallic green film, and deposits small, brownish-red, scaly crystals, which reflect light of a green colour. This potash-salt possesses the following properties. It is sparingly soluble in cold water, but dissolves completely in boiling water. The solution exhibits a pure purple colour, and this is so very intense, that a few particles of the dust, when dissolved by heat, suffice to give a fine red colour to a large quantity of water. Dilute alcohol also dissolves it.

When heated upon platinum, it detonates with rather a loud report, accompanied with a faint incandescence and a gray cloud. This decomposition occurs at about 328° F. When heated in a tube, the

report is very violent. Concentrated sulphuric acid also causes it to explode. The solution of this salt is precipitated by salts of silver, lead, mercury, and baryta. No precipitates are produced by salts of lime, strontia, zinc, or copper. Cyanogen cannot be detected in the solution of the potash-salt in the ordinary way.

If a concentrated solution of carbonate of potash be added to a moderately concentrated solution of the salt, a brownish-red, crystalline-pulverulent precipitate is quickly thrown down; but this, according to analytical experiments, is nothing but the same potash-salt, which only appears to lose in solubility by this addition. When the crude potash-salt, prepared as above, has not been very well purified by washing, it may happen that in the subsequent recrystallization it is only thrown down as a brown crumbly, indistinctly crystalline mass, with a green lustre. In this case it is dissolved again; the cooled solution is mixed with carbonate of potash, and the precipitate is collected and washed with cold water. When dissolved at a boiling heat, it is then readily converted into crystals.

Analyses were made with salt from different preparations dried at 212° F.,; they gave—

C	31·69	16	=96	31·46
H	1·49	4	4	1·31
N	22·65	5	70	22·93
O	..	11	88	28·83
KO	15·56	1	47·2	15·47

In order to ascertain, at any rate approximately, how much nitrogen is contained in the compound in any form other than that of NO^4, this was determined by ignition with soda-lime; 14·8 per cent. of nitrogen were obtained. Calculation gives 13·7 per cent. for 3 equivs. N.

Soda-salt.—This is formed by the reaction of cyanide of sodium upon picric acid. This salt is far more soluble than the potash-salt; the amount obtained, for this reason, and because its small capability of crystallization renders it difficult to purify, is but small. It is dark green with a metallic lustre; its solution is red.

Ammoniacal salt.—A concentrated solution of the potash-salt, on the addition of solution of muriate of ammonia, soon lets fall dark-coloured crystals of a metallic lustre, whilst the fluid becomes covered with a green film. The salt may be easily recrystallized, and forms, especially when crystallized from a not too concentrated solution, very beautiful, little, wedge-shaped crystals of a brownish-red colour, with a green surface colour. It dissolves very sparingly in cold water; but in boiling water it dissolves with a splendid intense purple colour. When heated upon platinum it explodes with fire, like gunpowder. The analyses of the salt dried at 212° F. gave—

C	33·86	33·36	33·99	16	=16	33·80
H	3·12	2·35	2·85	8	8	2·82
N	29·27	29·13	..	6	84	29·58
O	..	..	..	12	96	33·80

The determination of the nitrogen with soda-lime gave 19·03 per cent of nitrogen; N^3 being regarded as 2 (NO^4), there remains by calculation for N^4, 19·70 per cent.

Baryta-salt.—The solution of the pure potash-salt gives a precipitate of nearly a cinnabar colour with chloride of barium; this is but sparingly soluble in cold water, but dissolves completely in hot water with a purple colour.

When dried, it acquires a splendid, light green metallic lustre; when triturated, during which operation it becomes somewhat electric, it again appears red. It explodes with a dazzling green light.

If concentrated hot solutions of cyanide of barium and picric acid be mixed together, the fluid becomes blood-red, just as when cyanide of potassium is employed; a dark precipitate separates immediately, which is but sparingly soluble in cold water. When dried it has a beautiful reddish-brown colour, but is neither crystalline, nor entirely soluble in boiling water. The portion thrown down from the hot solution is a purple-brown powder with a green lustre; the undissolved portion effervesces with acids, and no doubt contains much carbonate of baryta. Analyses of the substance dried at 212° F. gave—

C	28·69	16	96	28·69
H	1·56	4	4	1·20
N	20·41	5	70	20·92
O	..	11	88	26·30
BaO	22·78	1	76·6	22·89

The determination of nitrogen with soda-lime gave 12·87 per cent. of nitrogen. Theory requires for N^3, 12·55 per cent.

Lime-salt, $C^{16}H^4CaN^5O^{12}+3HO$.—A hot saturated solution of the ammoniacal salt mixed with a solution of chloride of calcium gives no precipitate, but after standing for about 24 hours, deposits extraordinarily beautiful, metallic green needles of the lime-salt, which often attain a length of half an inch. At 212° F. they still retain 3 equivs. of water. Their analyses gave—

C	30·45	16	96	30·67
H	2·63	7	7	2·23
N	21·73	5	70	22·36
O	..	14	112	35·80
CaO	8·99	1	28	8·94

At 284° F. 0·449 grm. of this substance lost 0·0395 of water=8·79 per cent. Calculated for 3 equivs., 8·62 per cent.

Strontia-salt.—This was obtained by the decomposition of a solution of the potash-salt with nitrate of strontia, in the form of a precipitate, which, when dried, was pulverulent, indistinctly crystalline, and of a green lustre. It detonates with a red flame.

Silver-salt.—The brown precipitate which is produced by nitrate of silver in a solution of the potash-salt dries, after washing, into a dark green mass with a metallic lustre; it explodes when heated, and dissolves in much boiling water with a purple colour. The

analysis of the salt dried at 212° F. gave—

C	25·85	..	16 =	96	25·67
H	..	..	4	4	1·07
N	..	..	5	70	18·72
O	..	..	11	88	23·53
AgO	30·77	30·93	1	116	31·01

Lead-salt.—A solution of the potash-salt is pretty completely precipitated by a solution of acetate of lead. The precipitate, which is at first brownish red and very voluminous, becomes in a short time deep violet-brown and pulverulent (*a*). It dissolves in boiling water with a purple colour; the solution soon becomes coated with a bronze-coloured shining crystalline film, and deposits crystals, which, when examined under the microscope, are found to consist of extremely fine needles. After desiccation they are of a light brownish-red colour with a greenish surface lustre. When heated upon platinum they detonate very briskly.

When the crude lead precipitate (*a*) was stirred up with water and sulphuretted hydrogen was passed through it, it was only partially decomposed, although the fluid was saturated with gas. When the mass was boiled with water, a yellowish-red fluid ran off, which, on cooling, deposited brown tufts of laminar crystals, the analysis (*b*) of which showed that they had the same composition as the precipitate (*a*). They are very lustrous, but without any green tinge; they behave like the preceding when heated; their solution is dark golden brown. Analyses:—

	(*a*)	(*b*)			
C	25·46	..	16 =	96	25·98
H	1·53	..	4	4	1·08
N	..	18·36	5	70	18·94
O	..	..	11	88	23·83
PbO	29·80	29·83	1	111·5	30·17

Thus from the preceding salts we obtain as the formula of the acid contained in them, $C^{16} H^5 N^5 O^{12}$. The first thing that strikes us is that this is the formula of purpuric acid, which is derived from urea; and that, from this composition, the salts (for free purpuric acid is not yet known) are isomeric with the purpurates. It is interesting to see how far, with this equality in the amounts of the constituents, the chemical and physical resemblance also goes.

1. The acid of the salts investigated, which may be called *isopurpuric acid*, appears to be equally incapable of isolation with the purpuric acid from urea.

If a concentrated solution of the potash-salt, for example, be mixed with sulphuric acid, a decomposition soon occurs; the fluid changes its colour to brownish yellow, a penetrating odour is evolved, resembling that of acetic acid (cyanic acid?), but at the same time a trace of hyponitrous acid is detected, and brown amorphous flakes separate, such as often occur as products of the decomposition of the cyanides.

If it be filtered and evaporated, the residue freed by alcohol from

sulphate of potash, and the alcoholic solution evaporated, a certain quantity of a brownish- or orange-coloured deposit is produced, which exhibits nothing crystalline. The fluid filtered from this may be much concentrated without crystallizing, and finally a thickish, yellowish-brown, non-crystalline mass is obtained.

The attempt to separate the acid from one of the salts by the agency of other acids, both inorganic and organic (tartaric and oxalic acids), was repeated and modified frequently, but always produced a deeper decomposition. (For this reason also, beautiful as is the colour of the solutions of these salts, they cannot be employed in dyeing; without mordants they are neither beautiful nor durable, and they are rapidly destroyed on mordanted stuffs.) The reaction between the metallic salts and sulphuretted hydrogen, moreover, does not conduct us to the object, for it does not separate the whole of the metal, as is shown by the lead-salt.

2. The acid appears, like the purpuric acid from uric acid, to be bibasic. The last memoir by Beilstein upon this condition in purpuric acid, shows how difficult it is with that acid to prepare bibasic salts. The same difficulty occurs here.

Neutral isopurpurates appear to be formed—

a. When the solution of the potash-salt is brought in contact with solution of caustic potash. The fluid immediately acquires a splendid, deep violet colour, and a precipitate of the same colour is thrown down; a reaction, again, which exactly corresponds with that of purpurate of potash or murexide. The compound, however, could not be separated with sufficient rapidity. In a short time, very rapidly when heated, it becomes discoloured and finally brown. If it be evaporated, it leaves a deliquescent saline mass, which does not dissolve in alcohol. On the addition of a strong acid the phænomena described under 1 occur.

b. The ammoniacal salt behaves exactly like the potash-salt towards the caustic alkalies.

c. When the baryta-salt is triturated with baryta-water, during which process it becomes immediately of as beautiful a deep violet colour as the potash-salt. This is followed, however, just as rapidly by a discoloration and further decomposition.

d. When a solution of the potash-salt is mixed with an ammoniacal solution of silver, a brownish violet gelatinous precipitate of a basic salt is produced; this unfortunately presents great difficulties in purification. A very basic salt is also produced in this way from murexide (Beilstein).

3. The appearance of all the salts investigated resembles that of the purpurates in the highest degree. In their relative solubility, as far as it is possible to judge without quantitative experiments, there is scarcely any difference. The colour of the solutions is of the same beauty as that of the purpurates. The decomposition at a high temperature is only described as occurring in purpurate of silver, which detonates. The others also probably do likewise. All the isopurpurates detonate. (This circumstance frequently renders great care necessary in the analyses.)

4. The crystalline form and optical behaviour of some isopurpurates have been determined by Professor Grailich. According to him, isopurpurate of ammonia and murexide are exactly alike optically and crystallographically. In purpurate of ammonia the crystals are larger and more developed at the ends. It is, however, in both cases going too far to speak of a definite crystalline system. The outlines render the rhombic system the most probable; but then even the thinnest lamellæ must be absolutely opake for ordinary diffused daylight, such as is employed for the microscope; for neither with the purpurates nor isopurpurates could any appearance of colour be detected when the crystals were turned round between the crossed Nicol's prisms.

This is not improbable, because the remarkable green surface lustre is a certain characteristic of optical metallicity. The brown body colour in diffused light does not render a perceptible transparency necessary.

The potash compound appears to be isomorphous with the ammoniacal compound, but the laminæ are not so well crystallized; their outlines are seldom to be got, and they are all distinguished by a deep striation, which strikingly resembles that of the scales of butterflies. Some very fine laminæ, which appear pale brown by reflected light, are found, on closer examination, to owe their pale colour to the cooperation of the brown body colour with the metallic green surface tinge. The actual decision as to the crystalline system, both of murexide and of the two isopurpurates, can only be effected when either much finer laminæ or much larger crystals are prepared.

Isopurpurate of lime belongs to the rhombic system; a rhombic prism, the edges (probably macrodiagonal) of which appear to be truncated by broad pinakoid faces.

The ends of the crystals are never clearly developed; the prism usually breaks off with a dull and splintery terminal face set on at right angles, with regard to which one is in doubt whether it be actually a crystalline face.

Traces are seen, however, of (probably) brachydomes; to these also correspond the twin-crystals, often to be observed in very small aggregations, in which two prisms cross each other under angles of about 60°. The crystals, even in the smallest splinters, are almost absolutely opake. The body colour is a deep brownish red with a tinge of violet; by reflected light, a metallic green lustre with a tawny tinge makes its appearance, although no definite orientation of its polarization could be shown. If a somewhat broader and shining prism be broken in two pieces, and the fragments laid together crossing each other at right angles, the dichroscopic lens shows scarcely a trace of difference in the two pieces; in both cases the light appears, in accordance with the ordinary laws of reflexion, to be most intense and uniformly of a green colour for undulations at right angles to the plane of reflexion; very weak, and of a brownish colour for undulations in the plane of reflexion. However, the scaly surface of the faces of the crystals may essentially assist in veiling any dependence of the colour of the reflected light upon the orienta-

tion of the reflecting plane. The formation of isopurpuric acid may be simply expressed by the formula

$$\underset{\text{Picric acid.}}{C^{12}H^3N^3O^{14}} + 3(C^2NH) + 2HO = \underset{\text{Isopurpuric acid.}}{C^{16}H^5N^5O^{12}} + C^2O^4 + NH^3.$$

Free picric acid undergoes no change either in the cold or when heated by the action of hydrocyanic acid, but the reaction occurs immediately in the presence of a base.

It does not appear to be so easy to understand the intimate constitution of these compounds, as their mode of formation. To judge from the decomposition which they undergo by the action of acids, during which that penetrating odour, so strongly resembling that of cyanic acid, occurs, we might be inclined to suppose the actual presence of cyanic acid in them.

Under this supposition we should find a relation to isocyanuric acid. Schischkoff regards this as a cyanic acid combined with a nitro-substituted nitrile. We should then have

$$\left.\begin{matrix} C^4(H^2X)N \\ C^2HNO^2 \end{matrix}\right\} \qquad \left.\begin{matrix} C^{12}(H^3X^2)N \\ 2(C^2HNO^2) \end{matrix}\right\}$$

Isocyanuric acid. Isopurpuric acid.

and it is conceivable that if a nitrated formic acid were known, isocyanuric acid might be produced therefrom under similar conditions to those in which isopurpuric acid is formed from nitrated phenylic acid.

$$\underset{\text{Nitroformic acid.}}{C^2HNO^8} + 3C^2NH + 2HO = \underset{\text{Isocyanuric acid.}}{C^6H^3N^3O^6} + C^2O^4 + NH^3$$

$$\underset{\text{Trinitrophenylic acid.}}{C^{12}H^3N^3O^{14}} + 3C^2HN + 2HO = \underset{\text{Isopurpuric acid.}}{C^{16}H^5N^5O^{12}} + C^2O^4 + NH^3$$

On the other hand, it is very natural to seek for a connexion with picramic acid, which is produced from picric acid by reducing agents.

In fact the formula of isopurpuric acid is distinguished from that of picramic acid by the elements of cyanic acid:

$C^{16}H^5N^5O^{12}$ Isopurpuric acid.
$C^{12}H^5N^3O^{10}$ Picramic acid.

$C^4N^2O^2$ Cyanic acid.

Picramic acid could not, however, be found among the products of decomposition.—*Sitzungsberichte der Akad. der Wiss. zu Wien*, xxxv. p. 136.

White Brass. *By* M. Sorel.

A metallic alloy consisting of 10 parts of copper, 10 parts cast iron, and 80 parts of zinc, may be turned, filed, and bored, does not adhere to the moulds in casting, and retains its lustre for a very long time in moist air.—*Polytechn. Centralblatt*, 1859, p. 971.

Note upon Platinocyanide of Magnesium. *By* M. WERTHER.

The author has submitted to a fresh analysis both the red platinocyanide of magnesium, which always separates from the aqueous or dilute alcoholic solution during spontaneous evaporation in the exsiccator, and the yellow one which has been obtained with certainty by all the experimenters who have attempted its preparation with the exception of Weselsky. Schafarik's numbers for the amount of water in the red salt, and the amount of platinum in the anhydrous salt, do not agree well with the formula, and the amount of water in the yellow salt, according to Weselsky, does not coincide with the author's analytical data.

The amount of water in the red salt is without doubt 7 atoms. The author obtained 27·47 per cent. of water, corresponding with the formula MgCy + PtCy + 7 HO, which requires 27·9 per cent. Of this water 5 atoms escape at 302° F., and there remains the colourless salt, MgCy + PtCy + 2 HO, which becomes perfectly limpid and orange-yellow only at 408°—446° F. The further analysis gave—

Mg	5·04	1 = 12		5·47
Pt	43·30	1	98·94	43·60
Cy	..	2	52	23·03
HO	27·47	7	63	27·90

The yellow platinocyanide of magnesium is always obtained with certainty by the methods described by Weselsky, and is produced in the most beautiful form when a saturated solution is left to evaporate over sulphuric acid. The tolerably large, long, and flat prisms are perfectly stable in the air, and fluoresce under a blue cobalt glass with a green light, as intense as that of platinocyanide of barium, but in diffused daylight do not exhibit the bluish surface lustre presented by the latter salt.

Their composition is not, as Weselsky states, MgCy + PtCy + 6 HO, but they only contain 5 atoms of water, of which they lose 3 at 212°—302° F. At 212° F., and even up to 320° F., they did not lose more than 12·5 per cent., and up to 446° F. 8·7 per cent. more: calculation requires—

Mg	..	..		1 = 12		5·77	
Pt	..	..		1	98·94	47·58	
Cy	..	..		2	52	25·00	
HO	8·7	8·78		2	18	8·66	
HO	12·6	12·40	21·18	3	27	12·99	21·65

The amount of water found by Weselsky (22·6—22·7) agrees even better with the preceding formula than with the one established by himself.

Platinocyanide of magnesium exhibits even more than other compounds the influence of a definite amount of water upon the property of fluorescence; the red salt with 7 atoms and the white with 2 atoms of water do not fluoresce, but only that with 6 atoms. When, there-

fore, a writing on paper with the red salt is heated in order to obtain a writing adapted to the well-known experiments on fluorescence, and the temperature is raised about 122°—140° F., a negative result is obtained, because even at this temperature the conversion of the yellow salt into the white one takes place.—*Journ. für Prakt. Chemie*, lxxvi. p. 186.

On Hæmatoxyline. *By* O. Hesse.

In his investigation of hæmatoxyline, Erdmann arrived at the result that this body in combining with ammonia parted with hydrogen and took up oxygen. The formulæ established by Erdmann (for hæmatoxyline $C^{40}H^{17}O^{15}+8HO$, and for hæmateine $C^{40}H^{15}O^{16}$) were altered by Gerhardt, the former into $C^{32}H^{14}O^{12}+2HO$ and $+6HO$, and the second into $C^{32}H^{12}O^{12}$; and for the compound of hæmateine and ammonia Gerhardt assumed the formula $C^{32}H^{12}O^{12}$, $2NH^3$ (Traité de Chimie Organique, iv. p. 303). The latter formula of Gerhardt's does not agree with the results of analysis, for which reason the author repeated the investigation of this body.

He prepared the compound partly in accordance with the process described by Erdmann, and partly by the following process:—10—12 grms. of crystallized hæmatoxyline were put into a digesting flask, and dissolved in a quantity of ammonia insufficient for the formation of the compound of hæmateine and ammonia; the hot solution was filtered, when necessary, into a porcelain dish, which was left standing, loosely covered, in a cool place, and from time to time a little ammonia was added to it, as the fluid must constantly smell of ammonia. In two or three days the compound is usually crystallized. Any further increase of the mass of crystals is not to be expected, but it may afterwards become contaminated by non-crystalline substances. The fluid is poured away from the crystalline crusts, the residue of the mother-liquor is removed by washing, and the mass of crystals is then pressed as rapidly as possible between folds of bibulous paper. On account of its ready decomposability, the compound cannot be recrystallized. It gives off a large amount of water and ammonia when kept in the exsiccator; another portion of water is volatilized with ammonia at 212° F., and the weight becomes constant only at about 266° F., but at the same time every trace of ammonia is removed. The remaining blackish-violet powder possesses a greenish lustre, and is extraordinarily hygroscopic. It dissolves in aqueous ammonia with a splendid purple colour.

The purity of the compound submitted to analysis may be ascertained by boiling the substance with bisulphite of ammonia. If the substance be pure, a perfectly clear solution is formed.

Of the following analyses, I. to IV. are of the compound of hæmateine and ammonia, prepared according to Erdmann's process; V. to VII. of the substance prepared according to that described by the author. For analyses, I.—IV. the substance was dried for 6 hours *in vacuo* over sulphuric acid; for V. and VI. it had stood,

wrapped in bibulous paper, for one hour in the exsiccator; for VII. it was merely pressed between bibulous paper.

	I.	II.	III.	IV.	V.	VI.	VII.
C	..	..	55·36	55·12	..	51·49	
H	..	..	5·41	5·40	..	5·92	
N	3·59	3·58	..	..	3·74	..	3·66

The amounts of water contained in these different substances were determined by heating them to 266° F. At this temperature water and ammonia are evolved. By calculating the ammonia from the preceding analyses, and deducting it from the total loss, we get—

	I.–IV.	V.–VI.	VII.
Water evolved at 266° F.	4·34	4·54	4·44

The substance V. and VI., which was, in the author's opinion, best adapted for analysis, corresponds with the formula $C^{32}H^{9}(NH^{4})O^{10}+8HO$, which requires 19·41 per cent. of water. If all the substances be calculated for the same amount of water, namely 8 HO, we obtain the following numbers:—

	I. III.	II. IV.	V. VI.	VII.	$C^{32}H^{9}(NH^{4})O^{10}+8HO$.
C	52·07	51·85	51·68	..	51·75
H	5·74	5·73	5·89	..	5·66
N	3·37	3·36	3·76	3·72	3·77

By long standing over sulphuric acid the substance is decomposed in such a manner that its amount of ammonia is scarcely 1 per cent. The loss of water then appears to correspond with 5 equivs. The substance remaining when the ammoniacal compound is heated to 266° F. furnished the following numbers:—

	$C^{32}H^{10}O^{10}$	Experiment.
C	68·08	67·66
H	3·54	3·50

so that it has the centesimal composition of sublimed alizarine. The compound of hæmateine and ammonia, whose composition has just been given, has the same properties ascribed to his compound by Erdmann.

Bisulphite of ammonia produces a gelatinous precipitate in a solution of this compound; boiling causes this precipitate to disappear.

Solutions of chloride of potassium, chloride of ammonium, and especially of chloride of sodium, produce amorphous precipitates in an aqueous solution of the compound which is not too much diluted; these are of different colours according to the precipitant. Hyposulphite of soda produces neither decolorization nor precipitation.

In conclusion, the author indicates the possibility that hæmateine may be the

$$\text{anhydrous acid } \left.\begin{matrix} C^{32}H^{10}O^{8} \\ C^{32}H^{10}O^{9} \end{matrix}\right\} O^{4},$$

and Erdmann's hæmateine, the hydrate of this anhydride,

$$\left.\begin{matrix} C^{32}H^{10}O^{8} \\ H^{2} \end{matrix}\right\} O^{4};$$

the two ammoniacal salts would then be

$$\left.\begin{matrix} C^{32}H^{10}O^{8} \\ (NH^{4})^{2} \end{matrix}\right\} O^{4} \text{ (Erdmann), and } \left.\begin{matrix} C^{32}H^{10}O^{8} \\ H, NH^{4} \end{matrix}\right\} O^{4} + 6\,HO \text{ (Hesse).}$$

Liebig's *Annalen*, cix. p. 332.

On the presence of Butyric Acid in several substances in which its existence has not yet been indicated, and especially in Soils, in Stagnant Waters, and in the drainage of Dung-hills. *By* M. Isidore Pierre.

From the time when Chevreul published the results of his researches on the fatty bodies, butyric acid attracted but little attention, until MM. Gelis and Pelouze showed that this acid may be formed abundantly at the expense of sugar in the presence of putrefactive organic matters. About the same period Prince Charles Bonaparte ascertained the presence of the same acid in the waters of tanneries. Four years ago the author examined some bad cider, the use of which had greatly disordered the health of the people drinking it; he found that it contained a considerable quantity of butyric acid, and this was the only substance to which its effects upon the consumers could be attributed. He has since again ascertained the production of this acid in cider, and has seen the lees of that liquid thrown out so impregnated with butyric acid that it might have been prepared from them in great abundance. The acid is also frequently met with in the soil of cider-cellars, especially under the taps. The author likewise ascertained its presence in the water which had been used for washing two samples of earth which had received no manure for at least four years; one of these samples was taken within a depth of 20 centims. from the surface at eight different spots in the field; the other from the same places, but from a depth of from 20 to 40 centims.

In March 1859, M. Coillieux, a veterinary surgeon, called the attention of the Agricultural Society of Caen to a case in which a number of horses had been rendered seriously ill by the use of unwholesome water, and two of the number had died. The horses drank from a pool in the farm-yard; and M. Coillieux mentioned other analogous cases which had occurred in his experience. The analysis of the water of this pool showed a cosiderable quantity of butyric acid in a saline form. For this the author could not at first account; but on closer inquiry he found that some frozen beet-roots had been thrown upon the dung-hill, not far from the pond, and that these, under the influence of the rains, must have furnished the pool with a portion of their altered juices. Butyric acid was present in the juice pressed out of one of these beet-roots. The water of the pool contained no other substance so unwholesome that the accidents which had taken place could be ascribed to it. The author has since detected

butyric acid in all the brown waters of farm-yard pools that he has examined, and this was the more abundant the more easy the access of the manure-water. The latter often contains bytyric acid in large quantities, even without any apparent addition of saccharine matter which might favour its production.

The existence of this acid being ascertained, its production may be explained without difficulty. Saccharine matters are found in nearly all vegetables, in the straws of cereal plants, and in the fodder consumed in farms. A portion of these saccharine matters escapes assimilation and is restored in the fæces of the cattle; they must therefore occur in considerable amount in the dung-hills; and MM. Verdeil and Risler have ascertained their presence even in the soil of the Agronomic Institute at Versailles. These saccharine matters finding the necessary ferment in the manures, may be more or less completely converted into butyric acid.

The author mentions that in Normandy, when water is to be added to the juice of the apples in preparing cider, the country people have a notion that the water of ponds is preferable for this purpose to that of clear springs. As pond water is shown to contain butyric acid, the materials necessary for its formation (sugar and decomposing organic matters), the source of the butyric acid in cider is thus rendered clear.—*Comptes Rendus*, August 22, 1859, p. 286.

On a new Mode of Formation of Ferridcyanide of Potassium.
By Franz Reindel.

The author some time since described several double cyanides which are produced by the action of alkaline bases upon ferridcyanide of potassium in the presence of a reducing agent (such as sugar of milk, grape-sugar, and sulphurous acid). These salts have the general formulæ—

$$\left.\begin{matrix}3R\\M\end{matrix}\right\}4Cy, 2FeCy, \text{ and } \left.\begin{matrix}2R\\M\\X\end{matrix}\right\}4Cy, 2FeCy.$$

The author has now obtained another series of double salts of the formula

$$\left.\begin{matrix}2R\\2M\end{matrix}\right\}4Cy, 2FeCy.$$

These are produced—

a. By the neutral decomposition of Liebig's salt of potassium and barium and an alkaline sulphate; for example,—

$$\left.\begin{matrix}2K\\2Ba\end{matrix}\right\}4Cy, 2FeCy + 2NH^4O, SO^3 = \left.\begin{matrix}2K\\2NH^4\end{matrix}\right\}4Cy, 2FeCy + 2BaO, SO^3;$$

b. By treating ferridcyanides $\left.\begin{matrix}2R\\M\end{matrix}\right\}3Cy, 2FeCy$ with the base

MO and grape-sugar or milk-sugar:—

$$\left.\begin{matrix}2R\\M\end{matrix}\right\}3Cy, 2FeCy + MO = \left.\begin{matrix}2R\\2M\end{matrix}\right\}4Cy, 2FeCy + O.$$

c. By digesting the white substance of Williamson with an alkaline base; for example,—

$$\left.\begin{matrix}2K\\2Fe\end{matrix}\right\}4Cy, 2FeCy + 2NH^4O = \left.\begin{matrix}2K\\2NH^4\end{matrix}\right\}4Cy, 2FeCy + 2FeO.$$

As by ozonized or active oxygen (that just set free from an oxide) the ferrocyanide of potassium is rapidly converted into ferridcyanide, it must occur to us in considering the first of these three equations, that ferridcyanide of potassium must be formed from Liebig's salt by an alkaline bisulphate in the presence of a body capable of giving off oxygen:—

$$\left.\begin{matrix}2K\\2Ba\end{matrix}\right\}4Cy, 2FeCy + KO, 2SO^3 + O = 3KCy, Fe^2Cy^3 + 2BaO, SO^3.$$

This process takes place in a few minutes even in the cold, when peroxide of manganese is employed as the oxidizing agent. In the same way ferridcyanide of potassium is quickly formed from the ferrocyanide by sulphuric acid and peroxide of manganese.

The author takes this opportunity of correcting a statement formerly made by him with regard to ferridcyanide of sodium. Bette states that this salt forms ruby-red prisms which deliquesce in the air; Kramer, on the contrary, describes the crystals as green, transparent columns, which effloresce in the air. By long observation of ferridcyanide of sodium prepared by him, agreeing in colour and crystalline form with that described by Bette, the author found, that, according to the degree of humidity and the temperature of the air, it attracts moisture and effloresces. — *Journ. für Prakt. Chemie*, lxxvi. p. 342.

On the Action of Lime upon the Utricular Tissue of Plants. *By* E. Frémy.

In a preceding memoir the author announced, that by submitting certain membranes of plants to the action of lime he produced an acid soluble in water, and the energy of which might be compared with that of malic, citric, and tartaric acids. To this acid he gave the name of *cellulic acid*. He has since been enabled to operate upon a large quantity of beetroot, and in the present communication he gives the results of his last investigations of the acid produced by the action of lime upon the tissues of plants.

He first ascertained that all the utricular membranes of plants do not produce a soluble salt when treated with lime; this property is peculiar to those which contain *pectose*. When vegetable membranes have been submitted to the action of alkalies or of acids, and thus furnished pectine or pectic acid, they lose the faculty of producing the soluble lime-salt.

These facts clearly establish the relations existing between the gelatinous substances of plants and the acid under consideration; they show that these bodies are derived from the same immediate principle.

By operating upon vegetable membranes very rich in pectose, such as the pulp of beetroot, the author has prepared great quantities of the acid in a pure state by the following process:—the pulp is washed with distilled water and heated for an hour with boiling milk of lime; the mass is then pressed, the fluids evaporated to the consistence of a syrup and mixed with alcohol, which precipitates the lime-salt; the latter is decomposed by oxalic acid; the crude acid thus obtained is saturated with ammonia; and the ammoniacal salt is treated with acetate of lead, which throws down traces of colouring matter, phosphoric acid, &c. The liquid, when filtered, is rendered ammoniacal, when a very abundant white precipitate is formed, which, when decomposed by sulphuretted hydrogen, furnishes the pure acid.

This body presents the following properties. It is soluble in water in all proportions; its taste is decidedly acid; it decomposes all the carbonates and saturates the most energetic bases; its alkaline salts are not precipitated by solutions of lime, baryta, strontia, copper, &c.; when hot they reduce the salts of silver and Frommherz's reagent; in neutral and basic acetate of lead they produce precipitates which are soluble in an excess of the reagent.

From these characters the author recognized the acid as being identical with one described by him in a former memoir under the name of *metapectic acid*. The elementary analysis and the capacity of saturation of the acid confirmed this view.

Thus the acid produced by the action of lime upon the pulp of fruits and roots is a derivation of pectine; it is the last term of the series of gelatinous bodies of plants; its formula is

$$C^8 H^5 O^7, 2HO.$$

The production of metapectic acid under these circumstances is interesting in many respects, and leads to the following consequences.

Hitherto metapectic acid, which, from the simplicity of its formula and its general properties, may be compared with the most important organic acids, such as lactic, malic, and citric acids, &c., could only be prepared with difficulty. Now it may be prepared quickly and easily by the process above described.

The author has previously shown that metapectic acid is produced by the action of bases and acids upon pectine and pectic acid, but he was far from thinking that of the bodies forming this series of organic bodies, pectose, which is the first term, is that which has most tendency to produce metapectic acid, the last term. Ebullition for several hours is necessary to convert pectic acid into metapectic acid by the action of lime, whilst pectose is changed almost instantaneously by the action of bases.

These rapid modifications of the pectic compounds led the author

to think that the disappearance of the gelatinous principles which exist at a certain period in the tissues of plants may be due to the transformation of pectose into metapectates, and that these salts would be met with in considerable quantities in the juices of plants, and this view has been confirmed by analysis; the author has found alkaline or calcareous metapectates in all liquids possessing relations with the tissues containing pectose; the metapectates must therefore henceforward be included among the salts contained in the liquids that may be extracted from plants.

This formation of metapectic acid by the action of bases upon the tissues is of importance even in manufactures; in fact the author's recent investigations upon metapectic acid were undertaken especially in consequence of the difficulties experienced by a manufacturer of beetroot-sugar in the treatment of a juice produced by a new mode of manufacture, in which the pulps were submitted to the action of lime before being pressed; in this case the pulps may be pressed with facility, and the liquid quickly furnishes crystals of sugar, but the molasses retain a large quantity of lime which cannot be precipitated by carbonic acid. This is evidently due to the formation of metapectate of lime: it may be avoided to a certain point by only allowing the lime to act upon the pulp for a short time and at a low temperature.—*Comptes Rendus*, October 24, 1859, p. 561.

Contributions towards the Knowledge of the Chinone Group. *By* O. Hesse.

In this memoir the author communicates a series of experiments upon kinic acid, from which, as also from the investigations of Clemm upon the same acid, it appears that this acid is monobasic.

Free Kinic Acid, $C^{14}H^{12}O^{12}$, was separated from the lime-salt. This was decomposed by an excess of oxalic acid. The excess of oxalic acid was removed by acetate of lead, and the latter by sulphuretted hydrogen. The solution of the acid thus obtained was evaporated, and the acid obtained by crystallization. To purify it, the acid was dissolved in a small quantity of boiling water, and obtained in the form of a crystalline powder by disturbed crystallization.

Like other non-volatile acids, the acid prevents the precipitation of the metallic oxides, as Liebig had already discovered. It is not homologous with tartaric acid, from which it differs in its formula by C^6H^6. At 311° F. it could not be brought to a constant weight; at 329° F. it lost about 10 per cent. of water, and this quantity appears to be loosely combined water. At 428° F. it lost more than 13 per cent. of water, without becoming brown. The fused acid becomes soft, like pitch, when exposed to moist air; and if it had lost about 10 per cent. of water, crystals of an acid reaction soon made their appearance when water was poured over the fused mass. These were obtained of great beauty when kinic acid was heated to 482° F., by which means, however, a brown colour was

produced. The fused mass was dissolved in boiling alcohol, and the brown solution left to get cool, when an inconsiderable quantity of a brown mass was deposited, and this was removed. During the spontaneous evaporation of the alcoholic solution, crystalline groups, resembling muriate of ammonia, were deposited; these, when collected and recrystallized from water, were obtained colourless. They were readily soluble in both cold and hot water, and less soluble in dilute alcohol; they possessed an acid reaction, and their solution gave no colour with perchloride of iron, whilst the mother-liquor exhibited a dark-green colour with that reagent. The analyses of these two substances gave—

C	48·7	48·3	14=84	48·28
H	6·0	5·9	10 10	5·75
O	..	..	10 80	45·97

The substance, $C^{14}H^{10}O^{10}$, just described forms no salts, but when in contact with bases becomes again converted into kinic acid, $C^{14}H^{12}O^{12}$. It is probably the same substance that Baup has described as free crystallized kinic acid.

Kinate of Lime, $C^{14}H^{11}CaO^{12}+10HO$, was prepared,—1. by recrystallizing the commercial salt; 2. from a solution acidulated with muriatic acid; and 3. from a solution containing an excess of kinic acid. It always contains 6·6—6·7 per cent. of calcium, and 29·6—29·9 per cent. of water of crystallization. An acid salt is not formed. The lime-salt loses its water of crystallization completely at 248° F.

The salt dried at 248° F. loses nothing in weight up to 356° F., and does not become brown even at 392° F.

If the salt, $C^{14}H^{11}CaO^{12}+10HO$, be rapidly heated to 212° F., it fuses in its water of crystallization, which is combined with different degrees of force. Thus 7 HO are given off in the exsiccator. The salt, $C^{14}H^{11}CaO^{12}+10HO$, also very speedily loses 1 HO in the air, and passes in consequence to $C^{14}H^{11}CaO^{12}+9HO$, which again loses water, although but slowly.

Saccharate of lime, when dropped into a moderately concentrated solution of kinate of lime, produces a white, slimy precipitate, which, however, disappears when the fluid is agitated. An excess of saccharate of lime causes the solution to solidify. The white pasty mass emits a distinct sound when crushed with a glass rod, and is nothing but separated saccharate of lime. A compound of the formula $C^{14}H^{10}Ca^{2}O^{12}$ could not be prepared.

Kinate of Silver, $C^{14}H^{11}AgO^{12}$, was obtained by dissolving carbonate of silver in a solution of kinic acid. It bears a temperature of 212° F. without decomposition. It contains no water of crystallization (Gerhardt ascribes to it 2 atoms). Its analysis gave—

C	28·2	14	28·09
H	3·7	11	3·67
Ag	35·7	1	36·12
O	..	12	32·12

Æthylokinic Æther, $C^{14}H^{11}(C^4H^5)O^{12}$, was prepared by treating kinate of silver with iodide of æthyle. It is a tenaciously fluid body at ordinary temperatures, becoming very mobile at 122° F.; it possesses a faint aromatic odour and an extraordinarily bitter taste. It dissolves readily in water and alcohol, but with more difficulty in æther; it is gradually decomposed by water. When heated upon platinum-foil, a great part of it evaporates with formation of a white smoke; the last residue burns with a luminous flame. At about 464°—482° F. the æther appears to distil in a current of carbonic acid, but even at a few degrees above 212° F. a violent frothing and considerable loss occurs. Kinic æther heated to 284° F. in the air lost considerably in weight; it then had an acid reaction, and contained 49·3 per cent. of carbon and 6·8 per cent. of hydrogen. The analysis of the pure æther gave the following numbers:—

C	48·8	18	49·09
H	7·5	16	7·27
O	..	12	43·64

Basic Copper-salt, $C^{14}H^{10}Cu^2O^{12}+4HO$.—The author prepared this salt by treating kinic acid with hydrated peroxide of copper, and also by the far more advantageous method recommended by Liebig and others by means of kinate of baryta, sulphate of copper, and baryta-water. The salt prepared in either way, and dried in the air, contains from 1 to 2·5 per cent. of hygroscopic water, from which it may be freed in the exsiccator. It then possesses the composition given by Liebig, which may be expressed by the above formula. Gerhardt ascribed to this salt the formula $C^{28}H^{20}Cu^2O^{22}+2CuO+8HO$. The author assumes that at ordinary temperatures the copper-salt has the formula $C^{14}H^{11}CuO^{12}+CuHO^2+H^2O^2$, which, however, at 212° F. becomes converted into $C^{14}H^{10}Cu^2O^{12}$.

Aniline Compound.—If kinic acid be heated to about 356° F. with an excess of aniline, water and a portion of aniline distil over. On cooling, the mass solidifies with a laminar crystalline structure. By treatment with æther the portion of aniline still uncombined may be extracted, and after the crystals have been dissolved in a mixture of alcohol and æther, white, silky needles, grouped concentrically, are obtained, partly on the cooling of the fluid, and partly during its gradual evaporation; these dissolve readily in water and alcohol, but with difficulty in æther; when dried over sulphuric acid, they still retain water, which they give up at 194° F. without melting. The substance dried at 194° F. fuses at 345° F. without loss of weight, and solidifies at the same temperature, forming a mass with a laminar structure. It appears capable of bearing a temperature of 464° F., but cannot be sublimed without alteration. The analysis of the substance dried at 194° F. gave—

C	58·5	26	58·42
H	6·5	17	6·33
N	..	1	5·24
O	..	10	30·01

The analysis of the compound dried over sulphuric acid gave—

C	54·5	26	54·74
H	6·7	19	6·66
N	..	1	4·91
O	..	12	33·69

As this compound has a neutral reaction and represents a kinate minus 2HO, it is to be regarded as an anilide, which, in case kinic acid were bibasic, must be $C^{38}H^{22}N^{2}O^{8}$; this formula requires 66·66 per cent. C and 6·43 per cent. H, which does not agree with the numbers found.—Liebig's *Annalen*, cx. p. 333.

Observations on the Nitrates of Iron. By A. Scheurer-Kestner.

When the solution of a nitrate of iron is left to itself for a sufficient time, it sometimes sets into a jelly and appears to become turbid. By diluting the liquid thus modified with water, the jelly disappears, and a liquid is obtained which is limpid by transmitted and turbid by reflected light, having much analogy with the acetate of iron modified by heat, discovered by Péan de Saint-Gilles.

The allotropic modification of oxide of iron was obtained by means of acetate of iron, by exposing this salt to a heat of 212° F. With the same view, the author has submitted to the action of boiling water, neutral nitrate of iron and the two soluble basic nitrates of which he has described the properties and mode of preparation. These salts were enclosed in sealed tubes and plunged into a water-bath which was kept boiling. In a few hours the colour of the two basic salts was considerably modified, having passed from brownish red to brick-red; the solution was limpid by transmitted, turbid by reflected light. On opening the tubes, no odour of nitric acid was manifested, but the basic salts had acquired fresh properties. A drop of muriatic or sulphuric acid, or of a solution of sulphate of soda or potash, caused a precipitate in it; whilst, before being submitted to the action of heat, these salts were only precipitable by concentrated sulphuric or muriatic acid, and not at all by sulphate of soda. After 10 hours' boiling a portion of the tribasic nitrate, $Fe^{2}O^{3}, NO^{5}$, separated from the precipitate formed by means of sulphate of soda, gave the following numbers on analysis:—

NO^{5}	17·60
$Fe^{2}O^{3}$	9·88
Water	72·52

The oxide of iron and nitric acid are here in the proportion of 1 : 1·781, whilst originally the proportion was :: 1 : 0·68. After exposure for 72 hours to heat, the liquid separated from the precipitate as before had the composition of nitrate of iron with 3 equivs. of acid. At this point the action of heat stops; the neutral nitrate was not modified even by exposure to 212° F. for 144 hours. The two basic salts alone are therefore capable of modification.

The precipitate obtained with sulphate of soda, when dried upon biscuit-porcelain and in a current of dry air, forms small black

laminæ, which are insoluble in concentrated acids, but very soluble in pure water, reproducing a solution which is turbid by reflected and limpid by transmitted light. This remarkable solution no longer gives the characteristic reactions of iron-salts with the ferrocyanides and sulphocyanides; it may be precipitated again by acids and sulphate of soda, reproducing soluble oxide of iron. This oxide by calcination gave numbers closely approaching those of M. Péan de Saint-Gilles:—

Fe^2O^3	89·88
HO	10·12

The formula Fe^2O^3, HO requires

Fe^2O^3	89·89
HO	10·11

Oxide precipitated by 144 hours' ebullition.

Fe^2O^3	91·70
HO	8·30

Thus heat exerts upon the two basic nitrates an action analogous to that which it produces upon acetate of iron, except that while acetate of iron is decomposed completely into oxide of iron and acetic acid, the basic nitrates are decomposed into oxide and neutral nitrate, the latter resisting decomposition.

Light exerts the same action as heat upon these bodies, and it is to this agent that must be attributed the decompositions sometimes produced in solutions exposed to the air for some time. Three bottles, properly stopped, and containing the three soluble nitrates, were insolated for five months (from the 21st of December 1858 to the 21st of May 1859). The neutral nitrate preserved its original limpidity and composition, whilst the two basic salts were modified to a great extent. Even after an exposure of three months the liquids had become precipitable by sulphuric acid and sulphate of soda. The same salts kept purposely in the dark for the same time underwent no change.

Thus there is a considerable difference between the decomposition which these salts undergo at the heat of boiling water, and that produced by their own ebullition; in the one case they are decomposed without losing any elements, in the other they split into a more basic salt and free acid which escapes.—*Comptes Rendus*, June 27, 1859, p. 1160.

On the employment of Sulphurous Acid and the Alkaline Sulphites as a means of reducing the Persalts of Iron. By H. Buignet.

I. When 1 equiv. of pure and chemically neutral perchloride of iron is treated with 1 equiv. of sulphite of soda in solution, a blood-red colour of wonderful intensity is produced at the moment of mixture. This colour, however, very speedily disappears, and together with it the tint proper to the salt of iron, and in the course of a short time the mixture only presents the light greenish colour characteristic of the protosalts of iron. If the proportion of the equivs.

has been well observed, the reduction is complete, and the whole of the alkaline sulphite is converted into sulphate:—

$$Fe^2 Cl^3 + NaO\ SO^2 + HO = Fe^2 Cl^2 + NaO\ SO^3 + HCl.$$

II. If, before the addition of the alkaline sulphite, the perchloride of iron be mixed with variable and progressively increasing quantities of muriatic acid, the phænomena of coloration and decolorization become less and less distinct, and the reduction cannot be completely effected. The proportion of perchloride which escapes reduction is larger in proportion to the quantity of acid that has been added.

The influence exercised by muriatic acid is so great, that when its proportion is 10 equivs., that is to say, about 25 cubic centims. to 1 grm. of iron in the state of perchloride, the reaction obtained is scarcely more than one-fourth of that which it ought to be theoretically.

Although this result only applies to cases in which concentrated solutions are employed, it is nevertheless important as regards the testing of iron by Margueritte's process; for it shows the necessity of either diluting the liquids or saturating the free acid, in order to avoid serious errors.

III. The red colour manifested in the mixture of the neutral fluids is due in all probability to the formation of a sulphite of iron, $Fe^2 O^3, 3\,(SO^2)$.

The author has observed,—

1. That the same phænomena of coloration and decolorization may be produced by the direct action of sulphurous acid in solution upon hydrated sesquioxide of iron.

2. That by mixing the alkaline sulphite and perchloride of iron at the temperature of an ice-bath, by which means a little more stability is given to the red compound, the mixture at the moment contains neither sulphuric acid nor protoxide of iron.

IV. The protosulphite of iron, which is formed directly by mixing sulphurous acid and hydrated sesquioxide of iron, loses its red colour, becoming reduced into equal equivs. of sulphate and sulphite of protoxide of iron, at the same time that 1 equiv. of sulphurous acid is set free,

$$Fe^2 O^3, 3\,(SO^2) = FeO\ SO^3 + FeO\ SO^2 + SO^2.$$

Supposing that this is the mode in which the reduction of the persalts of iron is effected by the alkaline sulphites, it is very easy to explain the action of muriatic acid, by the obstacle which it presents to the combination of the sulphurous acid with the susquioxide of iron.—*Comptes Rendus*, Oct. 24, 1859, p. 587.

On the Formation of Oxalic Acid from Alcohol by Perchloride of Platinum. *By* J. Schlossberger.

The author found that oxalic acid was produced in a solution of perchloride of platinum in æther and alcohol which had been kept for a long time.—Liebig's *Annalen*, cx. p. 247.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Chemical Examination for Copper and Lead of Samples of Arrack, Rum, and Sugar, with Experiments on the Best Means of removing these Metals when existing in Spirits used for Drinking Purposes. *By* F. A. Abel, *Chemist to the War Department**.

The object to be attained by the chemical examination of samples of arrack, rum, and sugar forwarded from Ceylon to this country, by direction of Staff-Surgeon Alexander Smith, and referred to Mr. Abel for report by the Secretary of State for War, was to ascertain whether and to what extent, lead and copper existed in the samples in question.

Corresponding examinations, for comparative purposes, were also made of well-authenticated samples of Jamaica, Demerara, and Mauritius sugar of different qualities obtained from brokers in London, and of specimens of "Navy" rum obtained from the victualling yards at Portsmouth, Plymouth, and Deptford.

The methods employed for the examination of the samples of sugar and spirit were as follows:—

1. *Examination of the Samples of Rum and Arrack.*—The spirit, in quantities varying from three pints to one gallon, was concentrated by careful distillation to about one-fourth its volume; then evaporated to a viscid consistence on a water-bath, and finally transferred to a porcelain crucible and gently evaporated to dryness. The residue was ignited, with addition of a little nitric acid, and the ash afterwards digested with hydrochloric acid, in which it dissolved, with the exception, in some instances, of a minute quantity of flocculent matter. The solution was neutralized with carbonate of soda, acidified with acetic acid; a small quantity of bichromate of potassa

* From a Report to the Secretary of State for War, on the Results,—1. of a Chemical Examination for copper and lead of samples of arrack, rum, and sugar, collected in Ceylon by Staff-Surgeon Alexander Smith, M.D.; 2. of a similar examination of other samples of rum and sugar obtained in this country; 3. of experiments made to trace the effect of the use of Metal Stills on the purity of a spirit, such as arrack; and 4. of experiments on the best means for the removal of copper and lead when existing in spirits to be employed for drinking purposes.

was then added, and the liquid set aside for some hours. If a precipitate of chromate of lead was formed, it was collected, dissolved in hydrochloric acid; tartaric acid and excess of ammonia were added to the solution, through which hydrosulphuric acid was then passed. The precipitated sulphide of lead was collected and weighed as sulphate of lead, into which it was converted in the usual manner*.

The solution from which lead had been separated was mixed with a few drops of hydrochloric acid, and treated with hydrosulphuric acid; the precipitated sulphide of copper was dissolved in nitrohydrochloric acid, the solution mixed with excess of carbonate of soda, and the precipitate collected and weighed as oxide of copper.

2. *Examination of the Samples of Sugar.*—The solution of the sugar in a considerable quantity of distilled water, was mixed with hydrosulphuric acid-water, until it smelt powerfully of the gas, some egg-albumen was then thoroughly mixed with it, and the liquid was heated to ebullition. The coagulum, containing the metallic sulphides, was collected and incinerated in a muffle, the ash was digested with hydrochloric and a small quantity of nitric acid, and the solution evaporated; the residue was again boiled with hydrochloric acid, the solution filtered, and the insoluble portion thoroughly washed. The liquid, nearly neutralized with ammonia, was treated with hydrosulphuric acid, the resulting precipitate was dissolved in nitric acid, the solution neutralized with ammonia, and the lead and copper separated from it, and their proportions determined, in the manner above described.

The following results were obtained in the examination of the samples of spirit:—

Description of samples.	Amount of metals discovered in grains per Imperial gallon.	
	Copper.	Lead.
Arrack from Ceylon.		
Unmarked	·77	·06
Tavern in Galle	·57	Trace.
No. 37 Still	·75	None.
Commissariat stores, Newera Ellia	·75	Minute trace.
No. 48 Still, Bentotte	·40	·05
Do. do.	·32	None.
No. 21 Still, 12 miles from Galle	·64	None.
Rum from Ceylon.		
Unmarked, colourless	·14	None.
Montclair's Estate, Shandon	·51	None.
Paradua Estate, 1853	Trace.	None.
Rum from Admiralty Stores.		
Portsmouth, Clarence Yard	·03	Minute trace.
Plymouth	Trace.	None.
Deptford	·10	Trace.

* A little iron was occasionally precipitated as phosphate, together with the chromate of lead, in which case the precipitated sulphide of lead was digested with very dilute hydrochloric acid before ignition with nitric and sulphuric acids.

The samples of Ceylon spirits having been for a considerable time in bottle, it was necessary to determine whether any deposit, containing the metals searched for, had been formed in the bottles. Several of them were therefore rinsed out with nitric acid, but only minute traces of lead and copper were afterwards discovered in solution. The whole of the metallic impurities contained in the spirits at the time they were bottled, therefore, still remained in solution at the period of the examination.

The results of examination of the samples of sugar from Ceylon and of West Indian sugars obtained in this country, are given in the following Table, which also includes the results obtained by Professors Thomson, Hofmann, and Graham in the examination of ordinary sugars and treacle of commerce instituted by them, for the Board of Inland Revenue, in 1850.

Description of samples.	Metal contained in grains per pound.	
	Lead.	Copper.
Winter's Estate, Galle	None.	Slight trace.
Perodynia, 1854	Trace.	·07
Montclair's, Shandon, first quality	None.	Trace.
Do. do. lowest quality	·07	Trace.
Mr. Gardetti's, first quality	None.	None.
Do. lowest quality	None.	None.
Paradua Estate, first quality, 1854. For Ceylon market	·38	Faint trace.
Paradua Estate, first quality, 1854. For English market	·31	None.
Native Sugar Estate	None.	·03
SAMPLES FROM LONDON BROKERS.		
Jamaica, highest quality	Minute trace.	Minute trace.
Do. lowest „	·04	·016
Demerara, highest „	·027	·016
Do. lowest „	Minute trace.	·016
Mauritius, lowest „	Minute trace.	Traces.
SAMPLES EXAMINED BY PROFESSORS THOMSON, HOFMANN, AND GRAHAM.		
Moist sugar, West Indies	·033	
Bastards	·032	·018
Do.	·043	·014
Treacle	·155	

The following conclusions were arrived at, from the analytical results:—

1. None of the samples of Ceylon arrack and rum contained a sufficient amount of lead to exert an injurious influence on the health of persons drinking, even regularly for some time, the spirits represented.

2. Copper existed in small quantities in the whole of the samples of spirits examined, and in three to the extent of 0·75 grain in

an Imperial gallon. It appears doubtful, however, whether even this proportion of copper would be sufficient to act injuriously on habitual consumers of the spirits.

3. Two out of three of the samples of "service" rum examined contained traces of lead, and minute quantities of copper were found in all. In every case, however, the proportions were less than the small amount found in the Ceylon samples.

4. Five out of the nine samples of sugar from Ceylon contained no lead whatever; in one the proportion was only minute, but in the remaining samples the quantity was very appreciable; in the Paradua sugars it amounted to between three- and four-tenths of a grain in one pound of suger. The existence of minute proportions of lead in moist sugar, and particularly in the darker varieties (which contain much treacle), is very general, as was shown by the examination of sugar-samples in 1850, already referred to, and also by the examination of the samples of sugar from Jamaica, Demerara, and the Mauritius, given in the above table. But the quantity of lead existing in the Paradua sugar is considerably above the average proportions found in sugars of low quality.

5. Copper was also found in the majority of the samples of sugar, but only in minute quantities. The proportion was, however, somewhat greater in two instances than that discovered in the Demerara, Mauritius, and Jamaica sugars.

Although, therefore, the proportions of metallic impurities in the samples of spirits and sugar were in some instances greater than those discovered in the superior descriptions of commercial rum and sugar, it is doubtful whether (excepting probably in the case of the Paradua sugars) these impurities were sufficiently considerable to exert an injurious influence on the system of persons partaking of the articles in question to the customary extent.

The symptoms described by Dr. Smith, in his reports on the epidemic which occurred among the troops at Newera Ellia in 1852, as having been exhibited by the patients suffering from colic, are so characteristic as to leave little doubt that they resulted from the effects of lead upon the system. Some results which Dr. Smith describes as having been furnished by certain tests, applied to samples of arrack and sugar at the time of the outbreak of colic, would indicate the presence of a much larger proportion of lead, or of lead and copper, than that found even in the Paradua sugar.

It would appear from these circumstances that the degree of contamination, with lead, of the sugar or spirit, or of both, used at that period at Newera Ellia, must have been to a great extent exceptional, as believed by Dr. Smith, and that the materials in question could not be correctly represented by the samples above referred to.

The second part of the Report is devoted to an examination into the causes of impregnation of sugars with lead, and into the evidence existing, of the injurious effects of minute quantities of lead taken continually into the system.

Evidence is adduced of the frequent employment of lead in con-

nexion with different parts of the apparatus used at the Ceylon sugar-works, and of an occasional great want of care and cleanliness in the use of that metal; and it is shown that these circumstances cannot fail to lead to the occasional impregnation of the sugar (particularly of the darker descriptions) with lead to a dangerous extent. An instance is selected from the samples examined (the sugar from the Paradua Estate), in which the proportion of lead was undoubtedly sufficient to produce injurious effects upon persons partaking of it constantly for some time.

It is proved by the results of the examinations instituted, that manufacturers cannot be too seriously cautioned to avoid, as far as possible, the use of lead in any form, and that, where its employment is inevitable, the strictest care and cleanliness are indispensable.

The third part of the Report gives the results of an inquiry into the probable causes of the impregnation with lead and copper of the arrack prepared, and used by the troops, in Ceylon.

Although none of the samples of spirits examined, furnished evidence of contamination to any injurious extent, the fact, that Messrs. Redwood and Savory, in a report on samples from Ceylon, examined by them, in connexion with this inquiry, in September 1853, speak of the amount of lead in one sample of arrack as sufficient to be inimical to health, indicates that this spirit may be liable, under some conditions, to acquire an injurious proportion of lead in its manufacture.

From information collected in Ceylon by Dr. Smith, with regard to the method of preparing arrack, it appears very likely that an injurious impregnation of the spirit with lead frequently arises from the employment of defective apparatus and from the use of materials of a dangerous character in its preparation. A solder is often applied to the construction and repair of the copper stills and condensing worms, which consists of two parts of tin and one of lead. The stills vary in capacity from 20 to 160 gallons, and they are lined throughout with an alloy, which should consist of copper and tin only, but which almost always contains one-eighth, at least of lead. When properly applied, the coating should last three years, but it is said most generally to require renewal every year.

The circumstances attending the preparation of arrack from the juice of the cocoa-nut palm inevitably give rise to the production, with the spirit, of a very considerable proportion of acetic acid. The juice (or so-called toddy), after it has flowed from the flowering stalk of the plant, is kept in vats for from two to four days. The mean temperature of the district where the manufacture is carried on is about 80° F. Fermentation therefore proceeds with rapidity, and soon passes from the alcoholic to the acetic. The toddy has frequently been converted into vinegar in eight days.

It appears, moreover, that the period at which the fermentation is arrested and the liquid distilled, varies very considerably, being entirely dependent upon the time in which a sufficient quantity is collected to fill the stills. Thus, by the time that the last portions

of toddy are added to the first, in the vat, the latter have sometimes been standing for seven or eight days.

To produce the arrack of commerce, one quarter of the volume of fermented juice is distilled over, and this is subjected to redistillation, one-half its volume being collected.

It is evident that the acidity of a spirit prepared under these circumstances is liable to be very considerable. Ample proof of this is furnished by the results of examination of the samples of arrack received, which gave the following numbers:—

Description of Sample.	Grains of acetic acid in an Imperial gallon.
Unmarked	72
From tavern in Galle, used by soldiers prior to November 1854	46
No. 37 Still, Galle District	63·5
Commissariat store at Newera Ellia, used in 1852, and after June 1854	73·5
No. 21 Still, 12 miles from Galle	80
No. 48 Still	57

Little doubt can be entertained that spirits of such acidity as even the least acid of these, when distilled in retorts and condensers of copper, in which also lead exists as a constituent of solder, or of a tinning material, must acquire very estimable proportions of these metals, and particularly, as must always be the case, when the stills and worms are only periodically employed.

Unless these are cleaned with great care, their internal surfaces must, during the intervals between the operations, become partially or entirely coated with the products of the corrosive action exerted by the remnants of the last distillation which cling to the metal, and these products must enter more or less completely into solution in the next charge of acid spirit distilled.

On considering the nature of the action of acid vapour upon such metals as copper and lead, it appeared possible that a corrosion of these, and the consequent impregnation of the distilled spirit with them, might take place during the distillation, even if the still and worm were perfectly clean and bright at the commencement of the operation.

An experimental inquiry was therefore instituted, with the view to determine, as far as possible, the conditions under which copper and lead, and also alloys of these metals, are acted upon either by the vapour of an acid spirit during its passage from the still to the condenser, or by the liquid itself while it remains in the still, and the extent to which the corrosion will take place under different circumstances.

Experiments were made, in the first instance, with a model arrack-still of copper, received from Ceylon, of the exact form used in that country,—the interior of the body being lined with an alloy of lead and tin, and the head lined with tin only. The worm, which was

also copper, and consisted of several pieces brazed together, was not coated in the interior. Its surface was found to be oxidized to so considerable an extent as to preclude its employment in any experiments. The still-head was very flat and low, and therefore ill calculated to prevent the contamination of the products of distillation by portions of the liquid in the still which are continually thrown up when the former is boiling, and which, unless the head be high and of a form adapted to favour their retention and return to the body of the still, will be to a great extent carried over into the neck by the rush of the vapour, and thus pass into the condensed product.

The interior of the still was cleaned by distilling, first, considerable quantities of water acidified with acetic acid, and afterwards pure water. Three pints of arrack, already freed from metallic impurities by careful distillation, were afterwards distilled with moderate rapidity, the vapour being allowed to pass from the neck into a glass condenser. The greater portion having been distilled over, the product was examined and found to contain very appreciable quantities of copper and lead, and a minute quantity of tin. The residual liquid contained a very considerable amount of metallic impurities.

Repetitions of this experiment, with acidified spirit, furnished similar results; and when the head of the still was replaced by a glass head, the product also contained lead, copper, and tin, though the proportions of the two latter metals were less than in the preceding cases.

These results, and particularly the existence of lead in the products of distillation, which metal could only have been derived from the body of the still, prove that spirit distilled from vessels of this character and construction unavoidably acquires impurities from admixture with portions of the liquid, carried over from the still by the vapour during distillation.

A different form of still-head, of at least double the height of that at present in use, in proportion to the body of the still, and presenting no important difficulties of construction to the native tradesman, is described and recommended for adoption.

In experiments made with copper, tin, lead, tin-solder, lead-solder, brass, and an alloy of tin and copper, a spirit was employed which contained a proportion of acetic acid greater than that found in the arrack-samples examined, and approaching that which had been found to exist in an average-sample of the fermented palm-juice (*toddy*) from which the spirit is distilled. The strength of the spirit used was also regulated, so as to be somewhat below that of the distilled arrack.

The spirit was distilled from a capacious glass vessel, and the vapour allowed to pass into a long glass tube about three inches in diameter (constricted at the lower end) which served as a condenser. In this tube was placed, either in the form of thin sheet or in a granulated condition, the metal to be exposed to the action of the vapour and partially condensed product of distillation. In all

cases the surfaces of the metal were perfectly bright at the commencement of the experiments.

When it was deemed desirable, as far as possible, to exclude air, while the distillation continued, the tube condenser was tightly fitted to the neck of the glass still; but when air was to be freely admitted into the former during the operation, the still-neck was inserted loosely into the tube.

In order to determine the nature of action of the *liquid* on the metals composing the still, strips of these were placed in a glass flask containing the acid spirit, and fitted with a long vertical condenser, so as to allow the liquid distilling from the flask to return to it again. Air was made to enter the apparatus from time to time, by interrupting the operation occasionally, and allowing the flask to cool perfectly before heat was again applied. The strips of metal in the flask were only partially covered by the liquid.

The numerical details and results of the several series of experiments are given in the Report; the principal conclusions arrived at are as follows:—

1. The surface of the copper employed in the construction of the different parts of a still must on no account be exposed unprotected to the rapidly corrosive action which vapour and liquid of such acidity as arrack and toddy cannot fail to exert; such exposure, more particularly when intermittent (as in practice it will always be), would not only be speedily detrimental to the apparatus, but must inevitably lead to the impregnation of the distillate with copper.

2. Spirit or its vapour, containing a considerable proportion of acetic acid, exerts no action upon commercially pure tin which is in contact with it at a high temperature and in presence of air. Lead, on the other hand, is most powerfully acted upon by either, under similar circumstances.

When the vapour and partially condensed product of distillation of acid spirit pass over the surface of an alloy of lead and tin, both metals are dissolved, even when access of air is prevented as far as possible during distillation, the proportion of lead dissolved being generally considerable, and greater than that of the tin.

When an alloy of these metals remains for some time in contact with boiling acid spirit, with occasional admission of air, the lead is unquestionably dissolved in the largest proportion, in the first instance, but a secondary action ensues; the tin replaces the lead in solution, the latter being eventually precipitated in a spongy form.

3. The tin taken up by the spirit from the lining of a still does not remain very long in solution, as it is gradually converted into the binoxide of tin by any atmospheric oxygen with which the spirit comes in contact. To this fact, and to the ease with which small quantities of tin would be removed from solution by contact with the wood of the spirit-casks, the circumstance may probably be attributed, that no tin was discovered in any of the samples of spirit examined, although it must have existed in all the spirits, when freshly distilled, which were found to contain lead. It may, therefore, be safely concluded that the solution of small quantities

of tin by the acid, which may take place under peculiar circumstances, is not permanently prejudicial to the wholesomeness of the spirit.

4. It has been proved, however, that strongly acid spirit exerts no appreciable action upon tin, when that metal is exposed *alone* to its influence, and that a coating of tin upon copper will effectually prevent the action of the acid on the latter. Moreover, if any imperfection exist in the coating of tin, whereby portions of the copper surfaces are exposed to contact with the acid liquid, tin alone will be dissolved, and if the same liquid remain sufficiently long in contact with the metal, the portion of tin which has entered into solution will be again deposited, and will coat the exposed surface of copper; thus, in turn, preventing further action upon the tinned surface.

The results of the experiments have, therefore, satisfactorily established the perfect protection afforded to the interior of a copper still or condenser by a coating of tin, and have proved that tin, or an alloy of that metal with a little copper, should alone be used to coat *the whole interior* of an apparatus used for the distillation of an acid spirit like arrack. The employment of any alloy of lead as a material for coating, or the admission of any unprotected surface of copper, must interfere with the wholesomeness of the spirit, and should therefore be carefully guarded against.

5. The rapid action of acid spirit and its vapours upon the alloys of copper and zinc, which are occasionally used for brazing together portions of a still-apparatus, renders it most important that as small a surface as possible of that material should remain exposed in the interior of the still or condenser. By making the ends of the small well-tinned copper pipes, of which the still-worm should be constructed, to fit tightly one into the other, they might be readily joined by external brazing alone, and thus none of that material need be exposed to the action of the acid spirit.

The Report concludes with an inquiry into the possibility of effecting the separation of small quantities of copper and lead from their solution in an acid spirit, such as arrack; and the purifying effect, upon a spirit containing these metals, of simple contact, for some time, with wood which contains tannin, is experimentally established.

Process for Bleaching Palm Oil. By M. Rougier.

The palm oil is melted in a vat, and mixed with a certain quantity of brown oxide of manganese and a small quantity of muriatic acid, until complete decolorization takes place. The oil is then again freed from these additions. It is put into a chest lined with lead, on the bottom of which is a warm tube in which steam circulates; acidulated water is added to it, and it is heated until it separates from the stratum of water with which it has been washed.—Armengaud's *Génie Industr. Mag.*, 1859, p. 151; *and* Dingler's *Polytechn. Journal*, clii. p. 80.

On the Action of various Reagents upon Iodide of Potassium.
By G. Ubaldini.

When nitrate of ammonia and neutral iodide of potassium are intimately mixed at the ordinary temperature and in contact with the air, the mass acquires a yellow colour, and starch-paste, which acquires a blue tint, indicates free iodine in the mixture. The boracic acid of commerce acts in the same way. These two reagents, acting upon a concentrated solution of iodide of potassium at the temperature of ebullition, set free iodine.

By the action of contact aided by heat, operating with dry substances in a glass tube closed at one end, iodide of potassium is decomposed with evolution of violet vapours of iodine, not only by nitrate of ammonia and boracic acid, but also by sulphate, oxalate, carbonate, and muriate of ammonia, by phosphorus salt, sulphate, phosphate, nitrate, and borate of soda, chloride of sodium, chlorides of potassium and calcium, sulphates of potash and magnesia, nitrate of lime, and silicic acid.

The decomposition of iodide of potassium by the above mentioned substances, does not always take place at the same temperature; thus whilst silicic acid only decomposes the iodide at the temperature of fusion of glass, boracic acid, chloride of sodium, nitrate of ammonia, and nitrate of soda cause the evolution of the violet vapours at a low temperature. Oxalate of ammonia decomposes the iodide when it begins to decompose itself; carbonate and muriate of ammonia, when gently heated with iodide of potassium, fuse with it, forming a yellow liquid which evolves vapours of iodine in contact with the air; lastly, phosphorus salt, nitrate of lime, chloride of calcium, sulphate of ammonia, sulphate of magnesia, and sulphate, phosphate, and borate of soda, decompose iodide of potassium at a high temperature, and the violet vapours only make their appearance at nearly a red heat.

Sulphate, phosphate, and carbonate of lime, by the action of heat and air, partially decompose iodide of potassium; but binoxide of manganese, by the simple action of heat, eliminates all the iodine of the iodide.

Carbonate and nitrate of potash, and carbonate of soda have no decomposing action upon iodide of potassium.

Cantu announced the decomposition of iodide of potassium at a high temperature in a current of dry nitrogen, but this experiment repeated several times, never furnished the least evolution of violet vapours.—*Comptes Rendus*, August 22, 1859, p. 306.

Formation of Tartaric Acid from Sugar of Milk.
By J. von Liebig.

When the mother-liquor from the preparation of mucic acid from sugar of milk by means of nitric acid, is half neutralized with potash, it coagulates by the separation of bitartrate of potash.—Liebig's *Annalen*, cxi. p. 256.

On the Action of the Organic Chlorides upon the Hydrosulphate of Potash and Sulphuret of Potassium. *By* E. Jacquemin *and* Vosselmann.

In 1854, Kékulé, by the action of protosulphuret or persulphuret of phosphorus upon monohydrated acetic acid, obtained thiacetic acid, or hydrosulphate of acetyle. By the action of persulphuret of phosphorus upon anhydrous acetic acid, he also obtained anhydrous thiacetic acid, or sulphuret of acetyle.

The authors have arrived at the same result by another method which will render possible the production of the corresponding sulphurets of all the monohydrated acids, namely, by treating the hydrosulphate or the monosulphuret of potassium with an organic chloride. Thus—

$$C^{2n}H^{2n-1}O^2, Cl + \left.\begin{matrix}K\\H\end{matrix}\right\} S^2 = KCl + \left.\begin{matrix}C^{2n}H^{2n-1}O^2\\H\end{matrix}\right\} S^2,$$

or

$$2C^{2n}H^{2n-1}O^2, Cl + \left.\begin{matrix}K\\K\end{matrix}\right\} S^2 = 2KCl + \left.\begin{matrix}C^{2n}H^{2n-1}O^2\\C^{2n}H^{2n-1}O^2\end{matrix}\right\} S^2.$$

Hydrosulphate of Acetyle.—When 1 equiv. of chloride of acetyle is conducted, drop by drop, through a tube drawn out to a fine point, upon an equivalent proportion of hydrosulphate of potash placed in a retort provided with a receiver, the temperature rises and becomes sufficient to volatilize a portion of the chloride employed. By several distillations a yellowish liquid is at last obtained, which no longer contains any traces of chloride of acetyle. This rectified liquid distils almost entirely between 194° and 212° F.; by fractional distillation, a product boiling at 199°·4 F. is obtained. It presents all the properties of hydrosulphate of acetyle; it is colourless, and possesses an odour resembling at once that of sulphuretted hydrogen and acetic acid; it dissolves in water, and gives a white precipitate with acetate of lead.

Sulphuret of Acetyle and Lead.—This salt is easily produced by precipitating acetate of lead by the product of the preceding preparation.

Sulphuret of Acetyle.—This is prepared by heating together equivalent proportions of sulphuret of potassium and chloride of acetyle. Thus—

$$2C^4H^3O^2, Cl + \left.\begin{matrix}K\\K\end{matrix}\right\} S^2 = 2KCl + \left.\begin{matrix}C^4H^3O^2\\C^4H^3O^2\end{matrix}\right\} S^2.$$

It is a colourless liquid of an alliaceous and acetic odour; it boils at 248°—250° F., and is insoluble in water at first, but afterwardt disappears slowly by the action of this medium, which converts is into acetic acid and hydrosulphate of acetyle.—*Comptes Rendus*, Sept. 5, 1859, p. 371.

On the Volatile Oil of the Root of Valerian. *By* M. Pierlot.

Oil of valerian is contained ready formed in the root of *Valeriana officinalis*. The oil, whether fresh or old, contains about 5 per cent.

of valerianic acid. When rectified over potash it is neutral, and no more acid can then be separated from it by any reagent. It consists of two oils,—one of them has the formula $C^{20}H^{16}$, the other is an oxide of valerole $= C^{24}H^{20}O^4$, which is also neutral, and becomes resinified in the air and by the action of nitric acid. Valerole cannot be converted into valerianic acid.—*Comptes Rendus*, xlviii. p. 1018.

Investigation of Suberic Acid. By A. Riche.

Baryta has no action upon suberic acid in the cold, but when this acid is heated with an excess of baryta, a very brisk reaction takes place about 176° F.; white fumes are evolved, and a colourless or slightly yellowish liquid is condensed in the receiver.

If this be distilled, the greater part of the product boils at 169° F.; this, when analysed, presents the composition of the carburet of hydrogen, $C^{12}H^{14}$. This formula corresponds with 4 volumes of vapour; the vapour-density found was 3·17, the theoretical density is 2·97. The formation of this carburet is easily explained by the following equation:—

$$C^{16}H^{12}O^6, 2HO + 4BaO = C^{12}H^{14} + 4BaO, CO^2.$$

This compound is very mobile and refractive; its density at 78°·8 F. is 0·671. It possesses a faint aromatic odour; it is insoluble in water, but dissolves very readily in alcohol and æther. When a lighted taper is brought near it, it burns with a brilliant flame, bordered with blue. When a current of dry chlorine is passed into it, it becomes heated, evolves muriatic acid, and becomes viscous; bromine and iodine act upon it in the same way. Concentrated nitric acid acts upon it at the ordinary temperature, with evolution of red vapours, but the two liquids do not mix, as when benzine is acted upon by nitric acid; the carburet remains at the surface. Sulphuric acid gives it a slight violet colour.

The formula of this carburet seems to refer it to the series of carburets of which marsh-gas is the starting-point; but it is probable that it does not belong to this series, and that it is related to a family isomeric with the preceding. Thus the carburet, $C^{10}H^{12}$, which is the term immediately below it, boils at 86° F.; consequently the carburet, $C^{12}H^{14}$, should boil at about 122° F.; but we have seen that it boils at about 176° F.

The author has also ascertained directly that œnanthylic acid, $C^{14}H^{14}O^4$, when heated with an excess of baryta, does not furnish a product boiling at 167°—176° F., but a liquid whose boiling-point remains constant at about 131° F. This he is now investigating.

Nor is this body identical with æthylobutyle,—

$$\left.\begin{matrix} C^4H^5 \\ C^8H^9 \end{matrix}\right\} = C^{12}H^{14},$$

which was obtained by Wurtz by the action of sodium upon a mixture of iodides of æthyle and tetryle, for this latter compound boils at 134° F.

It is therefore probable that the series of bibasic acids, of which the known terms are—

Oxalic acid	$C^4 H^6$, 2HO
Succinic acid	$C^8 H^4 O^6$, 2HO
Pyrotartaric acid ..	$C^{10} H^6 O^6$, 2HO
Adipic acid	$C^{12} H^{10} O^6$, 2HO
Pimelic acid	$C^{14} H^{12} O^6$, 2HO
Suberic acid	$C^{16} H^{12} O^6$, 2HO
Sebasic acid	$C^{20} H^{16} O^6$, 2HO,

furnishes, under the influence of an excess of baryta, a series of carburets of hydrogen, isomeric but not identical with that furnished by the fatty acids, of which formic acid is the first term.—*Comptes Rendus*, August 22, 1859, p. 304.

On Compounds of Bismuth with Chlorine, Bromine, and Iodine. *By* R. Weber.

Terchloride of bismuth, the colour of which is usually described as yellow or greyish white, is snow-white when in a state of perfect purity. If it be heated with metallic bismuth, protochloride of bismuth is readily obtained. The mixture is sealed up in a glass tube and heated. For this purpose the metal is not used in the form of a powder, but in fragments; the excess then remains in the form of regulus, from which the protochloride may be more easily separated.

The protochloride thus obtained has all the properties ascribed to it by Schneider, who discovered it. It is of a brownish colour, readily fusible, and crystalline. It is decomposed by water, and at a high temperature it splits into perchloride and metal. Concentrated solution of muriate of ammonia likewise decomposes it. The analyses gave 75·3, 75·1, and 74·9 per cent. of bismuth, corresponding with the formula $BiCl^2$ (Bi=208).

If powdered bismuth be thrown into chlorine gas it forms terchloride of bismuth; but, on the contrary, when chlorine is allowed to find access slowly to powdered bismuth, the protochloride is first formed without any incandescence.

Terbromide of Bismuth, $BiBr^3$, was prepared by the author in the bulb-tube; one limb of this was bent down and sealed; it served as a reservoir for the bromine. The vapour of bromine was driven over the metal placed in the bulb. Bromide of bismuth distils off in the form of a red fluid, which solidifies into a sulphur-yellow crystalline mass. It is fusible with more difficulty than the corresponding chloride, and acquires a transitory red colour at a high temperature. Nitric acid dissolves it readily with decomposition. Metallic bismuth acts upon it; and it may be concluded with some probability that there is a protobromide corresponding with the protochloride above described.

Teriodide of Bismuth, BiI^3, is readily obtained by throwing small quantities of iodine upon bismuth strongly heated in glass tubes. The crude product is distilled without access of air, and the per-

iodide is then obtained as a shining black mass with a laminar structure. The periodide prepared in the humid way, when distilled, passes into iodide of bismuth in the same condition; but at the same time there is formed some basic iodide, and iodine is set free.

The perchloride is reduced not only by bismuth, but also by other bodies, such as phosphorus, zinc, tin, mercury, and silver.—Poggendorff's *Annalen*, cvii. p. 596.

On the Equivalents of Manganese and Nickel. *By* R. Schneider.

The author publishes two series of experiments upon the equivalents of manganese. The first was carried on by Rawack in the author's laboratory. In these experiments the quantity of water was determined which was furnished by a known quantity of pure protoxide of manganese when calcined in pure hydrogen.

The second series of experiments was made by Schneider himself. In this the proportion between carbon and pure protoxalate of manganese was determined. The numbers obtained are as follows:—

	Rawack.	Schneider.
1.	27·052	27·008
2.	27·029	27·028
3.	26·999	27·023
4.	27·025	27·015
5.	26·942	
6.	27·005	
Mean	27·009	27·019

In consequence of an objection raised by Marignac to the accuracy of the author's determination of the atomic weight of nickel, he has again determined the equivalent of that metal by the same process that he formerly adopted. By the analysis of neutral oxalate of nickel, he ascertained the proportions of carbon and nickel in that salt. The average of three experiments gave

29·029
29·025 (previously),

so that he again arrived at the whole number 29.

The author then enters into some considerations as to the determination of equivalents in general. Here he expressly states that he considers the opinion that different elements have the same atomic weight as not yet proved, and also raises objections to the proportions lately established by Dumas, according to which certain atomic weights are of $\frac{1}{4}$ atom and others of $\frac{1}{2}$ atom of hydrogen.—Poggendorff's *Annalen*, cvii. p. 605.

On the highest Sulphuret of Arsenic. *By* H. Rose.

Wackenroder first stated that the so-called pentasulphuret of arsenic was a mixture of sulphur and tersulphuret of arsenic, because

when sulphuretted hydrogen is passed into the aqueous solution of arsenic acid, sulphur is first precipitated, and then tersulphuret of arsenic, AsS^3. This view was lately confirmed by Ludwig and now by Rose, who indicates that this may also be the case with pentasulphuret of antimony, and many other precipitates produced by sulphuretted hydrogen. If the compounds AsS^5 and SbS^5 actually exist, it does not follow that these compounds are capable of being isolated.—Poggendorff's *Annalen*, cvii. p. 186.

On the Humoid Constituents of the Cinchona Barks.
By O. Hesse.

In the investigation of the Huanoco Cinchona bark Reichel found a brown matter, the properties of which differed from those of humic acid of peat, and to which he gave the name of lignoine.

Analyses of lignoine dried at 212° F., made by Hesse, gave

C	59·4	59·2	40	59·25
H	6·1	5·6	23	5·67
N	3·5	..	1	3·47
O	..	..	16	..

Lignoine, $C^{40}\,H^{23}\,NO^{16}$, dissolves very readily in alkaline carbonates, and these solutions absorb no oxygen; in other respects it differs but little from the humoid substances.

The nitrogen expressed in the preceding analysis is contained in the form of ammonia, which is set free by boiling with caustic potash, when a body of the composition $C^{40}\,H^{20}\,O^{16}$ is obtained. This body, therefore, is distinguished by its composition from the humoid bodies of vegetable mould and peat, as it contains four atoms of hydrogen more than of oxygen.

The Chinova-red prepared by Hlasiwetz has the same composition as the substance when free of ammonia. In this Hlasiwetz found

C	61·10	61·32
H	5·05	5·26

Phlobaphene also belongs here. For this body the formula $C^{20}\,H^{10}\,O^8$ was lately proposed. Reichel also obtained from red Cinchona bark a brown matter (which he calls a lignoine-like body) containing

C	61·15
H	4·65 (?)

The latter substance, however, contains some ammonia, as appears from Reichel's further experiments.

It consequently appears that a brown humoid matter of the same composition is deposited in the Cinchona barks, which may be expressed by the formula $C^{40}\,H^{20}\,O^{16}$. It is essentially distinct from the China-red of Schwarz, and not to be classed with this, as has

been done by Gerhardt. It is, however, remarkable, that in this humoid matter we again meet with the group $C^{20}H^{10}$, which makes its appearance if we attribute to quinine the formula

$$\left.\begin{matrix}(C^{2}H)^{20}\\(NH^{2})^{2}\end{matrix}\right\}O^{4}.$$

Liebig's *Annalen*, cix. p. 341.

On the employment of the Residue of Sulphate of Zinc from Galvanic Batteries, and on the treatment of Zinc-blende by the humid way. *By* M. Kessler.

When equal equivalents of sulphate of zinc and chloride of sodium are mixed together, the crystals formed below 50° F. are a double sulphate of soda and zinc, but at 32° F. they consist of pure sulphate of soda.

The mother-liquor may be advantageously used in the preparation of oxide of zinc.

Blende, when sulphatized and mixed with chloride of sodium and similarly treated, furnishes sulphate of soda and chloride of zinc, with which zinc white may be prepared.—*Comptes Rendus*, June 27, 1859, p. 1153.

On the Behaviour of Oil of Cloves to some Metallic Oxides.
By R. Böttger.

When perfectly dry oxide of silver is moistened with oil of cloves, the oil is inflamed almost immediately with scattering of sparks. This oil behaves in the same way with oxide of gold. With peroxide of lead and chloride of lime, the mixture only becomes heated, with evolution of fumes. Permanganate of potash and oxide of mercury are indifferent towards oil of cloves. The oil obtained from oil of cloves after the removal of the caryophyllic acid, does not possess the property above described.—Poggendorff's *Annalen*, cvii. p. 322.

Conversion of Cellulose into Parchment or Parchment-paper.

It appears that this curious product of the action of concentrated sulphuric acid on bibulous paper, by which means the paper is changed to a tissue very much resembling ordinary parchment, nearly as strong and resisting the action of boiling water, which parchment does not, is not a new observation, but was first made known in 1846 by Messrs. Poumarêde and Figuier in the Journal de Chemie et de Pharm. for 1847, under the name of *papyrine*.—Silliman's *American Journal*, Nov. 1859.

INDEX TO VOL. XVII.

Abel, on the detection of lead and copper in spirits and sugar, 461.
Acetal, conversion of, into aldehyde, 314.
Acetates, products of the dry distillation of, 389.
Acetic acid, on the synthesis of, 317; metamorphoses of, 361.
Acetone, 323; metamorphoses of, 361.
Acetones, products of the oxidation of the, 92.
Acetonitrile, action of cyanide of mercury on, 429.
Acetyle, behaviour of chloride of, to tartaric acid, 51.
Acroleine, action of acids upon, 356.
Æthal, new compounds of, 11.
Æther, action of chlorine upon, 149.
Æthers, on the action of different, upon sodium-alcohol, 311; hydrosulphocyanic, production of, 169; nitric, action of the hydrated alkalies upon, 349.
Æthyle, platinocyanide of, 41.
Æthylene, oxide of, 155.
Air, estimation of the organic matter of the, 176; action of, on mixtures of sulphide of calcium and carbonate of potash or soda, 286; method of analysing, 316.
Alcoholic alkalies, new mode of production of the, 194.
—— fermentation, on, 387.
Alcohols, on several new, 10.
——, polyatomic, on the combination of the, with the bibasic acids, 390.
Aldehyde, action of acids upon, 358.
Aldehyde-ammonia, on a new base produced by the decomposition of, 121.
Aldehydes, behaviour of the, with the acids, 356.
Alloxan, compounds of, with alkaline bisulphites, 205.
Alloys, on the specific gravity of, 320.
Allyle, selenio-cyanide of, 248.
Alumina, acetate of, 95; separation of phosphoric acid from, 315.
Aluminium, on the amalgamation and gilding of, 355.
Amarine, constitution of, 54.
Ammonia, caustic, manufacture of, 426.
Amylamine, action of bisulphide of carbon on, 196.
Amylosulphurous æther, 191.
Andira anthelminthica, on the resin of, 29.
Andrews, T., on ozone, 216.
Aniline, on the formation of, 126.
Anisic acid, salts of, 21; action of anhydrous sulphuric acid upon, 23.
Anthon, E. F., new method of preparing sulphurous acid, 105.
Antimony, perseleniuret of, 57.
Arbutine, constitution of, 48.
Arrack, on the detection of copper and lead in, 461.
Arsenic, detection of small quantities of, 439; on the highest sulphuret of, 474.
Arsenites, action of air on alkaline, 414.
Atropine, valerianate of, 9.
Barbet, M., on a method of distinguishing citric and tartaric acid, 292.
Barium, reduction of the chloride of, 165; alloys of, 165.
Baryta, non-precipitation of, by sulphuric acid, 57; solubility of the sulphate of, in nitrate and muriate of ammonia, 232; manufacture of sulphate of, 213.
Bases, organic, on a new class of, 218.
Béchamp, M., on the reduction of nitrobenzine by sodium-alcohol, 125.
Beilstein, F., on murexide, 13; on the action of different æthers upon sodium-alcohol and upon ethylocarbonic acid, 311; on the conversion of acetal into aldehyde, 314; on the isomerism of organic compounds, 341.
Beketoff, M., on a new method of forming chloride of benzole, 286.
Belhomme, M., on a colouring matter from *Paulownia imperialis*, 113.
Benzamic acid, action of nitrous acid upon, 199.
Benzole, new method of forming chloride of, 286.
Benzoylanilide, action of iodide of æthyle upon, 365.

Berthelot, M., on several new alcohols, 10; on the camphenic series, 27; observations on sulphur, 86; on the action of the hydrated alkalies upon the nitric æthers, 349.
Bichloracetone, 364.
Bile, on the colouring matter of the, and its detection, 221.
Birney, J., on the solubility of bone-earth in solutions of chloride of ammonium and common salt, 406.
Bismuth, separation of, from other metals, 117, 119; behaviour of basic nitrate of, to an aqueous solution of ammonia, 119; on the behaviour of oil of cloves to metallic oxides, 476.
Blood-spots, detection of, 212.
Bolley, Prof., on the amount of picric acid obtained from Botany Bay resin, 136; new compound of potassium, iron, copper, and cyanogen, 137; on the manufacture of chloride of lime and the preparation of caustic ammonia, 426.
Bone-earth, solubility of, in chloride of ammonium and common salt, 406.
Borodine, A., on the constitution of hydrobenzamide and amarine, 53; on the action of iodide of æthyle upon benzoylanilide, 365.
Boron, compounds of, 193.
Böttger, Prof. R., on the action of coal-gas upon various saline solutions, 261; on protochloride of palladium as a reagent for various gases, 290; compounds of, with chlorine, bromine, and iodine, 473.
Boussingault, M., on the relations of the soil to vegetation, 266.
Boutlerow, A., on dioxymethylene, 325.
Brass, white, 447.
Braun, G. J., on the preparation of murexide, 371.
Breton, M., on a process for depriving spirit of fusel oil, 160.
Brodie, Prof. B. C., on the atomic weight of graphite, 319.
Brücke, E., on the recognition of blood-spots, 212; on the colouring matter of the bile, and its detection, 221.
Brunner, C., on molybdate of ammonia, 106; on the separation of zinc from nickel, 113; on the behaviour of ammonia towards sulphur, 113; on the preparation of platinum-black, 146; on a new process for the determination of the amount of carbon in limestones, 175; on cleaning paint brushes, 215; on the determination of precipitates in analyses, 253; on cleaning glasses and capsules, 430.
Bryonine, 107; bryonitine, 108; bryoretine, 110.
Buckton, G. B., on the mercuric, stannic, and plumbic ethyles, 276.
Buignet, H., on the employment of sulphurous acid and the alkaline sulphites for the reduction of persalts of iron, 459.
Butylactic acid, 8.
Butyric acid, presence of, in the soil and in the drainage of dung-hills, 451.
Cadmium, separation of, from other metals, 117.
Calcium, alloys of, 165.
Callmann, H., on crystallized valerianate of atropine, 9.
Camphenic series, on the, 27.
Camphic acid, 28.
Camphol, new compounds of, 12, 28.
Canouil's processes for manufacturing chemical matches without phosphorus or poisonous substance, 214.
Carbon, on the determination of the amount of, in limestones, 175.
Carbonic acid, new apparatus for determining, 174.
—— oxide, action of, on sodium-alcohol, 238; on the cause of the formation of, in the volumetric determination of nitrogen, 291.
Carius, L., on the behaviour of the chlorides of sulphur towards amylic alcohol, 190.
Caron, H., on the reduction of the chlorides of barium, strontium, and calcium by sodium, and on alloys of these metals, 165.
Cartmell, R., on the behaviour of the aldehydes with the acids, 356.
Caseine, on a crystallized compound of, 72.
Cellulic acid, 453.
Cellulose, conversion of, into parchment, 476.
Cerium, salts of, 241; on the oxides of, and the yellow and red sulphates of its protoperoxide, 321.
Chinese green, on the preparation and properties of, 267.
Chinone group, new derivatives of the, 410, 455.
Chlorobenzole, on the action of ammonia upon, 69.
Chlorolactyle, 344.
Chloropicrine, metamorphoses of, 413.
Chloropropionic acid, 207.
Chlorous acid, preparation of, 136, 404.
Cholesterine, new compounds of, 11.

Chrome-yellow, 419.
Chromium, salts of, 81; phosphuret of, 229; observations on, 381; magnetic oxide of, 383.
Chrysolepic acid, new processes for obtaining, 1.
Chyle, presence of urea in, 342.
Cinchona barks, on the humoid constituents of the, 475.
Citric and tartaric acids, simple method of distinguishing, 292.
Cloëz, M., on the conversion of the nitrogen of nitrogenous matters into nitrate of potash, 15.
Coal-gas, action of, upon various saline solutions, 261.
Coals, bituminous, on some modified results attending the decomposition of, by heat, 167.
Cobalt, preparation of metallic, 225.
Copper, separation of, from other metals, 117; determination of, 211; formation of protoxide of, 283; detection of, in spirits and sugar, 461.
—— plates, on the coating of engraved, with iron, 353.
Creatine in the urine of dogs, 253.
Cresylic alcohol, preparation and derivatives of, 281.
Cumole, bibenzoate of, 49.
Cumylphenyle, 124.
Cyanides, action of the iodides of æthyle, methyle, &c. upon, 192.
Cyanoform, 421.
Cyanuric æther, 52.
Cynuric acid in the urine of dogs, 253.
Debray, M., on the fusion of considerable masses of platinum, 377.
Debus, Dr. H., on the oxidation of glycol, and on some salts of glyoxylic acid, 294.
Desplats, M., on the combination of the polyatomic alcohols with the bibasic acids, 390.
Deville, C. Sainte-Claire, on some modifications in the method of analysing air, 316; on the fusion of considerable masses of platinum, 377.
Dextrine, estimation of, 349.
Diabetes insipidus, on the absence of sugar in the urine of, 369.
Diazodinitrophenol, 198.
Dinitrocuminates, 124.
Dinitrocuminic acid and compounds, 147.
Dioxymethylene, on, 325.
Diphosphonium-compounds, on the, 234.
Donnell, J. M'., on the action of air on alkaline arsenites, 414.
Dowling, J., on the estimation of tannine, 430.
Duclos, L., on cresylic alcohol, 281.
Dumasine, 389.
Dyeing, improved process in, 233.
Eichler, W., on melampyrite and its compounds, 345.
Engelhardt, A., on the salts of anisic and nitroanisic acids, 21; on the action of ammonia upon chlorobenzole, 69; on sulphobenzamic acid, 127.
Erdmann, O. L., on hæmatoxyline, 227; on the solubility of sulphate of baryta in nitrate and muriate of ammonia, 232; on the formation of protoxide of copper, 283.
Ethylamine, new derivatives of, 397.
Ethylocarbonic acid, 312.
Fatty bodies, saponificatives of, by means of chloride of zinc, 158.
Ferridcyanides, 452.
Ferrocyanide of potassium and copper, 137.
Fibroine, 104, 371, 430.
Field, F., on the occurrence of Tagilite and Libethenite, as well as some combinations of lime, copper, and phosphoric acid, near Coquimbo, 223.
Fittig, Dr. R., on some metamorphoses of acetone and acetic acid, 361; on some products of the dry distillation of acetates, 389.
Frankland, Dr. E., on organo-metallic bodies, 254.
Frémy, E., on the salts of chromium, 81; on the action of lime on the utricular tissue of plants, 453.
Friedel, C., on the products of the oxidation of the acetones, 92.
Fries, E., on the behaviour of the chlorides of sulphur towards amylic alcohol, 190.
Fritzsche, M., on the combinations of the hydrocarbons with picric acid, 16.
Fusel oil, new process for depriving spirit of, 160.
Gases, reagent for various, 290.
Geisse, Dr. L., on chloropicrine, 413.
Gentele, J. G., on the determination of grape-sugar, cane-sugar, and dextrine, 349.
Geuther, Dr. A., on the electrolysis of sulphuric acid, 285; on the behaviour of the aldehydes with acids, 356.
Glasses and capsules, how to clean, 430.
Glyceritartaric acid, 391.
Glycol, on the oxidation of, 294; action of acids on, 298, 334.

Glycol, monohydrochloric, 156.
Glycols, on the, 157.
Glyoxylates, 295.
Gmelin, O., on solanine, 385.
Gorgeu, A., on the coloration of the salts of manganese, and on oxalate of manganese, 71.
Gorup-Besanez, E. von, on the action of ozone upon organic compounds, 401.
Graphite, atomic weight of, 319.
Griess, P., on new nitrogenous derivatives of the phenyle and benzoyle series, 198.
Guanine, on the conversion of, into xanthine, 151.
Guignet, M., on the conversion of the nitrogen of nitrogenous matters into nitrate of potash, 15.
Gypsum, removal of, from water, 60.
Hæmatoxyline, properties and constitution of, 227, 449.
Hart, P., on a method of estimating the nitrous acid contained in nitrous vitriol, 173; on a modification of Fresenius and Will's apparatus, 174.
Hayes, Dr. A. A., on the decomposition of bituminous coals by heat, 167.
Heintz, Prof., on a new base produced by the decomposition of aldehyde-ammonia, 121; on stasfurtite, 148; on two new derivatives of saccharic acid, 170.
Hempel, C. W., on the determination of mercury, 392.
Hesse, O., on some new derivatives of the chinone group, 410, 455; on cyanide of mercury and acetonitrile, 429; on hæmatoxyline, 449; on the humoid constituents of the Cinchona barks, 475.
Hippuric acid, quantitative determination of, 416.
Hlasiwetz, H., on a new mode of decomposition of trinitrophenylic acid, 441.
Hofacker, G., on seleniuret of sodium and antimony, 56.
Hofmann, Dr. A. W., on the phosphorus-bases, 96, 377; on the monamines, 196; on a new class of organic bases, 218; on the diphosphonium-compounds, 234; on new volatile organic acids, from the berry of the mountain ash, 273; on the poly-ammonias, 397.
Holzmann, Dr., on some salts of cerium and lanthanium, 241.
Hops, on the sulphuring of, 76.
Hydrobenzamide, constitution of, 53.
Hydrobryoretine, 110.
Indigo, action of the sesquisalts of iron on, 33.
Inosite, properties of, 26.
Iodide of potassium, action of various reagents upon, 470.
Iodine, on the estimation of, in kelp, and the approximate separation of iodine and chlorine, 137; new process for determining, 352; detection of small quantities of, 439.
Iron, nitrates of, 70, 458; on the reduction of the persalts of, 459; separation of phosphoric acid from, 315.
Isopurpuric acid and salts, 441.
Jacquemin, E., on the action of the organic chlorides upon the hydrosulphate of potash and sulphuret of potassium, 471.
Jonas, L. E., on the production of pictures by means of iodine and guaiacum resin, 226.
Juncadella, E., on the action of nitric æther upon iodide of potassium, 190; on the alcoholic alkalies, 194.
Kangaroo, on the bile of the, 425.
Kawalier, M., on the yellow colouring matter and the tannic acid in *Thuja occidentalis*, 61, 88.
Keller, F., on the constitution of scammony, 309.
Kelp, analysis of Highland "cutweed," 209; improvements in the manufacture of, 392.
Kessler, M., on the treatment of zinc blende, 476.
Kind, M., on solanine, 308.
Kinic acid, 455.
Knop, Dr. W., on the double cyanides of platinum, 94.
Kolbe, H., on the constitution of lactic acid, 343.
Krafft, L., on the saponification of fatty bodies by chloride of zinc, 158.
Kraut, Dr. C., on toluylphenyle and cumylphenyle, 123; on dinitrocuminic acid, 147.
Kromayer, A., on the colouring matter of the bark of the root of *Lithospermum arvense*, 154.
Lactic acid, conversion of, into propionic acid, 206; on the constitution of, 327, 343.
Lactobutyric acid, 328.
Lamont, J., analysis of Highland "cutweed" kelp, 209.
Lanthanium, salts of, 241.
Lea, M. C., on picric acid and some of its salts, 1.

Lead, separation of, from other metals, 117; detection of, in spirits and sugar, 461.
Lead-poisoning with snuff, 428.
Libethenite, 223.
Lieben, A., on the action of chlorine upon æther, 149.
Liebig, J. von, on oxalan, 145; on creatine and cynuric acid in the urine of dogs, 253; on the formation of tartaric acid from sugar of milk, 470.
Lignoine, 475.
Lime, manufacture of the chloride of, 426.
Limpricht, H., on cyanuric æther, 52.
Lithospermum arvense, on the colouring matter of, 154.
Lo-kao, preparation of, 267.
Löwe, J., on the qualitative separation of the oxides of mercury, lead, bismuth, copper, and cadmium, 117; on the behaviour of basic nitrate of bismuth to an aqueous solution of nitrate of ammonia, and on the separation of bismuth from some metals, 119.
Luca, S. de, on a new process for determining iodine, 352.
Lucifer matches without phosphorus, 214.
Ludwig, Dr. A., on the colouring matter of the bark of the root of *Lithospermum arvense*, 154.
Lymph, presence of urea in the, 342.
Magnesia, separation of, from potash and soda, 20.
Magnesium, platinocyanide of, 448.
Manganese, on the coloration of the salts of, and on oxalate of, 71; on solutions of sesquisalts of, 101; new process for determining the amount of pure peroxide of, in the native ore, 288; equivalent of, 474.
Martius, C. A., on compounds of boron, 193; on phosphuret of chromium, 229.
Maschke, O., on a crystallized compound of caseine, 72.
Matthiessen, Dr. A., on the action of nitric acid and of binoxide of manganese and sulphuric acid on the organic bases, 78; on the specific gravity of alloys, 320.
Meconine, stearate of, 12.
Meidinger, Dr. H., on the coating of engraved copper plates with iron, 353.
Melampyrite and compounds, 345.
Mendelejef, D., on œnantholosulphurous acid, 163.
Merck, W., on veratric acid, 66.
Mercurial bases, on the, 301, 329.
Mercuric ethyle, 276.
Mercury, decomposition of cyanide of, by the iodides of methyle, æthyle, and amyle, 19; separation of, from other metal, 117; volumetric determination of, 392.
Mesityle, on the oxide of, 363.
Metacroleine, 357.
Metallic sulphurets, on the decomposition of the, by chloride of phosphorus, 312.
Metapectic acid, 454.
Meteoric stone of Kaba, on the organic substance in the, 266.
Molybdate of ammonia, preparation of, 106; on the applicability of, as a test, 440.
Molybdenum, phosphide of, 208.
Monamines, on the, 196.
Moreau, M., on the determination of copper, 211.
Mottay, Tessié du, on the saponification of fatty bodies of chloride of zinc, 158.
Müller, G., on the quantitative determination of the amount of tannine in tanning materials, 115.
Murexide, on the nature of, 13; preparation of, on a large scale, 371.
Nachbaur, C., on the so-called cyanoform, 421.
Nickel, equivalent of, 474.
Ninaphtylamine, salts of, 218.
Niobium, nitruret of, 211.
Nitric acid, on the detection of, in solution, 31.
—— æther, on the action of, upon iodide of potassium, 190.
Nitroacetone, 365.
Nitroanisic acid, salts of, 23.
Nitrobenzine, on the reduction of, by sodium-alcohol, 125.
Nitrogen, determination of, 291.
Nitrogenous matters, on the conversion of the nitrogen of, into nitrate of potash, 15.
Nitrous vitriol, method of estimating the nitrous acid contained in, 173.
Nitroveratric acid, 67.
Nolte, G., on a new process for determining the amount of pure peroxide of manganese in the native ore, 288.
Œnantholosulphurous acid, 163.
Oil of bitter almonds, action of acids upon, 359.
—— of cloves, behaviour of, to metallic oxides, 476.
—— of Valerian, 471.

Ordway, J. M., on a new mode of making commercial caustic soda, 38.
Organic bases, action of nitric acid and of binoxide of manganese and sulphuric acid on the, 78.
—— compounds, on the isomerism of, 341.
Organo-metallic bodies, on, 254, 276.
Osann, M., on the preparation of anhydrous sulphuric acid, 166; on the detection of small quantities of arsenic and iodine, 439.
Oxalan, 145.
Oxalic acid, formation of, from alcohol, 460.
Ozone, on, 216; action of, upon organic compounds, 401.
Paint brushes, cleaning, from dried oil colours, 215.
Palladium, protochloride of, a reagent for various gases, 290.
Palm-oil, process for bleaching, 469.
Pappenheim, Dr. L., note on Steinbühl-yellow, 419.
Paracetone, 362.
Parchment-paper, 476.
Pasteur, L., on alcoholic fermentation, 387.
Paulownia imperialis, on a new colouring matter from, 113.
Peckolt, T., on andirine and the resin of *Andira anthelminthica*, 29.
Pelouze, J., on the manufacture of sulphate of baryta, 213; on the action of air on mixtures of sulphide of calcium and carbonate of potash or soda, 286.
Petersen, T., on Spanish zinc-bloom, 68.
Phenylamine, action of nitrous acid upon, 200; new derivatives of, 397.
Phosphammonium compounds, 377.
Phosphoretted ureas, 96.
Phosphoric acid, volumetric determination of, 229; new process for the separation of, from alumina and oxide of iron, 315.
Phosphorus, on some reactions of the pentachloride of, 249; decomposition of the metallic sulphurets by the perchloride of, 312.
Phosphorus-bases, researches on the, 96, 377.
Picramic acid, action of nitrous acid upon, 198.
Picric acid, preparation of, 136; salts of, 1; combinations of the hydro-carbons with, 16; action of hydrocyanic acid on, 447.
Pictures, production of, by means of iodine and guaiacum resin, 226.
Pierlot, M., on the oil of Valerian, 471.
Pierre, T., on the presence of butyric acid in soils and in the drainage of dung-hills, 451.
Pincus, Dr., on the volumetric determination of phosphoric acid, 229.
Pinitannic acid, 88.
Plants, action of lime on the utricular tissue of, 453.
Platinohydrocyanic acid, 42.
Platinum, preparation of the double cyanides of, 94; on the fusion of considerable masses of, 377.
—— black, preparation of, 146.
Plessy, M., on the determination of copper, 399.
Plumbic diethyle, 280.
Poly-ammonias, researches on the, 397.
Polygonum Fagopyrum, on a yellow colouring matter obtained from the leaves of, 201.
Precipitates, determination of, in analyses, 253.
Propionic acid, conversion of lactic acid into, 206.
Purpurates, preparation and constitution of the, 13.
Quercitrine, on the occurrence of, as a colouring matter in flowers, 161.
Rammelsberg, Prof., on the oxides of cerium and the yellow and red sulphates of its protoperoxide, 321.
Reindel, F., on a new mode of formation of ferridcyanide of potassium, 452.
Riche, A., on acetone, 323; on suberic acid, 472.
Rochleder, F., on the behaviour of chloride of acetyle to tartaric acid, 51; on the occurrence of quercitrine as a colouring matter in flowers, 161.
Rose, H., on the composition of the native minerals containing tantalic acid, 24; on solutions of sesquisalts of manganese, 101; on the isomeric modifications of peroxide of tin, 111; on nitruret of niobium, 211; on the highest sulphuret of arsenic, 474.
Roseochrome and compounds, 84.
Rougier, M., on a process for bleaching palm-oil, 469.
Royal Institution of Great Britain, proceedings of the, 176.
Royal Society, proceedings of the, 78, 96, 195, 216, 234, 253, 273, 294, 317, 334, 356, 377, 397.
Rue, on the constitution of the essential oil of, 130.
Rumicine, constitution of, 17.
Rutine, 204.

Sacc, M., on the application to dyeing of a new method of decomposing hypochlorite of lime, 233.
Saccharic acid, new derivatives of, 170.
Saint-Pierre, M., on the reduction of nitrobenzine by sodium-alcohol, 125.
Samaderine, 143.
Sarcine and salts of, 141.
Scammony, on the constitution of, 309.
Schafarik, A., on the compounds of vanadium, 181.
Schaffgotsch, G. G., on the separation of magnesia from potash and soda, 20.
Scheerer, T., on the non-precipitation of baryta by sulphuric acid, 57.
Scheurer-Kestner, A., on the nitrates of iron, 70, 458.
Schiel, Dr. J., on chlorous acid, 136, 404.
Schlagdenhauffen, M., on the decomposition of cyanide of mercury by the iodides of methyle, æthyle, and amyle, 19, 192; on the production of hydrosulphocyanic æthers, 169.
Schlossberger, J., on fibroine and the horny substance of sponge, 104; on the bile of the kangaroo, 425; on the fibroine of spider's threads, 430; on the formation of oxalic acid from alcohol by perchloride of platinum, 460.
Schneider, Dr. O., on the mercurial bases, 301, 329.
Schneider, R., on the equivalents of manganese and nickel, 474.
Schrötter, A., on the formation of carbonic oxide in the volumetric determination of nitrogen, 291.
Schulze, F., on the separation of phosphoric acid from bases, especially from alumina and oxide of iron, 315.
Schunck, Dr. E., on a yellow colouring matter from the leaves of *Polygonum Fagopyrum*, 201.
Seleniuret of sodium and antimony, 56.
Sericine, 430.
Sharswood, W., on the preparation of metallic cobalt, 225.
Siemens, Prof., on the sulphuring of hops, 76.
Silicium, on the direct formation of the nitruret of, 370.
Silk, on the chemical nature of, 371.
Simpson, Dr. M., on the action of acids on glycol, 298, 334.
Smith, Dr. R. A., on the estimation of the organic matter of the air, 176.
Snuff, on lead-poisoning with, 428.
Soda, improved processes for the manufacture of, 38, 287.
Soil, on the relations of the, to vegetation, 266.
Solanidine, 308, 386.
Solanine, 308, 385.
Sommer, C., on umbelliferone, 283.
Sorbic acid and salts, 274.
Sorel, M., on white brass, 447.
Spencer, T., on the manufacture of the Uchatius cast steel, 73.
Spider's threads, on the fibroine of, 430.
Spirits, detection of copper and lead in, 461.
Sponge, on the horny substance of, 104.
Städeler, G., on the applicability of molybdate of ammonia to the detection of phosphoric acid, 440.
Stanethyle, 255.
Stannate of soda, analysis of commercial 171.
Stannic diethyle, 278.
Stasfurtite, analysis of, 148.
Steel, Uchatius cast, on the manufacture of the, 73.
Steinbühl-yellow, 419.
Strecker, A., on arbutine, 48; on sarcine, 141; on the conversion of guanine into xanthine, 151.
Strontium, alloys of, 165.
Suberic acid, action of baryta upon, 472.
Succinic acid, presence of, in wine, 388.
Sugar, estimation of, 349; detection of copper and lead in, 461.
Sulphates, on the preparation of some pure, and particularly of sulphate of copper, 58.
Sulphoanisic acid, 24.
Sulphobenzamic acid, properties and composition of, 127.
Sulphobutyric acid, 367.
Sulphocyanides, 169.
Sulphoglycolic acid, 298.
Sulphovalerianic acid, 369.
Sulphur, on the modifications of, 86; behaviour of ammonia towards, 113; behaviour of the chlorides of, towards amylic alcohol, 190.
Sulphuric acid, on the preparation of anhydrous, 166; on the electrolysis of, 285.
Sulphurous acid, new method of preparing, 105; employment of, for reducing persalts of iron, 459.
Tagilite, 223.
Tait, P. G., on ozone, 216.
Tannecortepinic acid, 91.
Tannine, quantitative determination of the amount of, in tanning materials 115, 430.

Tantalic acid, on the minerals containing, 24.
Tartaric acid, simple method of distinguishing from citric acid, 292; formation of, from sugar of milk, 470.
Tetrelallylammonium, hydrated oxide of, 122.
Thann, K. von, on rumicine, 17; on platinocyanide of æthyle, 41.
Thiacetic acid and salts, 367, 471.
Thuja occidentalis, on the yellow colouring matter and the tannic acid in, 61, 88.
Thujine, preparation and properties of, 61; thujetine, 63; thujetic acid, 64.
Tin, on the isomeric modifications of peroxide of, 111.
Tissier, C., on acetate of alumina, 95; on the amalgamation and gilding of aluminium, 355.
Toluylphenyle, 123.
Trehalose, compounds of, 12.
Trinitrophenylic acid, processes for obtaining, 1; new products of the decomposition of, 441.
Tungsten steel, 292.
Tuson, R. V., on the absence of sugar in the urine of *Diabetes insipidus*, 369.
Tüttscheff, J., on bibenzoate of cumole, 49.
Ubaldini, G., on the reaction of various reagents upon iodide of potassium, 470.
Ulrich, Dr. C., on the conversion of lactic acid into propionic acid, 206; on thiacetic and sulphobutyric acids, 367.
Umbelliferone, on, 283.
Urea, presence of, in the chyle and in the lymph, 342.
Ureas, phosphoretted, 96.
Valerole, 471.
Vanadium, on the compounds of, 181.
Vegetation, on the relations of the soil to, 266.
Veratric acid, preparation and properties of, 66.
Veratrole, 67.
Vogel, A., jun., on the chemical nature of silk, 371.
Vohl, Dr. H., on the properties of inosite, 26.
Voit, E., on Spanish zinc-bloom, 68.
Vosselmann, M., on the action of the organic chlorides upon the hydrosulphate of potash and the sulphuret of potassium, 471.
Wakefield, W., on commercial stannate of soda, 171.
Wallace, Dr. W., on the estimation of iodine in kelp, and the approximate separation of iodine and chlorine, 137; on the manufacture of kelp, 392.
Walz, G. F., on *Bryonia alba*, 107.
Wanklyn, J. A., on the synthesis of acetic acid, 317; on the action of carbonic oxide on sodium alcohol, 238.
Weber, Dr. R., on some reactions of pentachloride of phosphorus, 249, 312; on compounds of bismuth with chlorine, bromine, and iodine, 473.
Werther, M., on the platinocyanide of magnesium, 448.
Wicke, W., on lead-poisoning with snuff, 428.
Williams, C. G., on the constitution of the essential oil of rue, 130.
Wine, presence of succinic acid in, 388.
Wislicenus, M., on a new base produced by the decomposition of aldehyde-ammonia, 121.
Wöhler, Prof., on the phosphide of molybdenum, 208; on selenio-cyanide of allyle, 248; on the organic substance in the meteoric stone of Kaba, 266; on the nitruret of silicium, 370; on chromium, 381.
Wreden, R., on the quantitative determination of hippuric acid, 416.
Wurm, F. X., on tungsten steel, 292.
Wurtz, A., on butylactic acid, 8; on oxide of æthylene, 155; on lactic acid, 327; on the presence of urea in the chyle and in the lymph, 342.
Wurtz, H., on the detection of nitric acid in solution, with observations on the action of sesquisalts of iron upon indigo and metallic gold, and on the neutralization of the colours of metallic solutions, 31; on the preparation of some pure sulphates, and particularly of sulphate of copper, 58.
Wuth, Dr., on compounds of alloxan with alkaline bisulphites, 205.
Xanthine, conversion of guanine into, 151.
Zinc, separation of, from nickel, 113.
Zinc-blende, on the treatment of, 476.
Zinc-bloom, on Spanish, 68.
Zincmethyle, 257.
Zwenger, Dr., on solanine, 308.

END OF VOLUME XVII.

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Chemical gazette.

v. 17

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